Review and advances of direct methanol fuel cells (DMFCs) part I: Design, fabrication, and testing with high concentration methanol solutions

Xianglin Li, Amir Faghri*

Department of Mechanical Engineering, University of Connecticut, Storrs, CT 06269, United States

HIGHLIGHTS

► The experimental studies on direct methanol fuel cells using high concentration methanol and pure methanol has been reviewed.
► Methanol transport, water management, oxygen transport, and carbon dioxide release in DMFCs have been analyzed.
► The improvements on DMFC design and the advances of DMFC stacks and prototype developments have been presented.
► Unresolved issues and challenges in DMFCs have been identified and reviewed.

ARTICLE INFO

ABSTRACT

A review of the experimental studies on passive and semi-passive direct methanol fuel cells (DMFCs) is conducted, with an emphasis on high concentration methanol and pure methanol. Key issues such as methanol transport, water management, oxygen transport, and carbon dioxide release in the DMFC are analyzed in detail. The design and fabrication, development approaches, challenges and opportunities on DMFCs passively fed with high concentration methanol are discussed. The advances of DMFC stacks and prototype developments are presented. Several unresolved issues and challenges in DMFCs are identified and reviewed in detail.
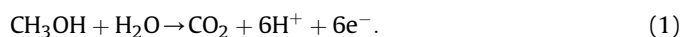
© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The rapidly growing market and the increasing complexity of small portable electronic devices such as smart phones, laptop computers, MP3 players, and GPS are two factors that have placed tremendous pressure on power supply systems. These increasing demands of power supply systems can no longer be fully met by the rechargeable lithium and nickel based battery systems currently used commercially due to their limited energy density. Furthermore, a rechargeable battery requires an external electrical power source for recharging. This is a severe limitation to the mobility of these devices, especially for applications in remote areas without readily available electrical sources. Significant efforts have been made to seek alternative power sources. Proton exchange membrane fuel cells (PEMFCs), electrochemical devices that convert chemical energy directly into electrical energy, are promising alternatives to rechargeable batteries.

One type of PEMFC, a direct methanol fuel cell (DMFC), uses methanol or methanol solutions as fuel and works at near room temperature. As shown in Fig. 1, methanol and water are oxidized in the anode catalyst layer (CL) and release electrons and protons during operation:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-. \tag{1}$$

The electrons are transported through an external circuit to the cathode while the protons penetrate the electrolyte membrane to the cathode. In the cathode CL, oxygen from the ambient air reacts with the electrons and protons and generates water:

* Corresponding author. Tel./fax: +1 5104864304.
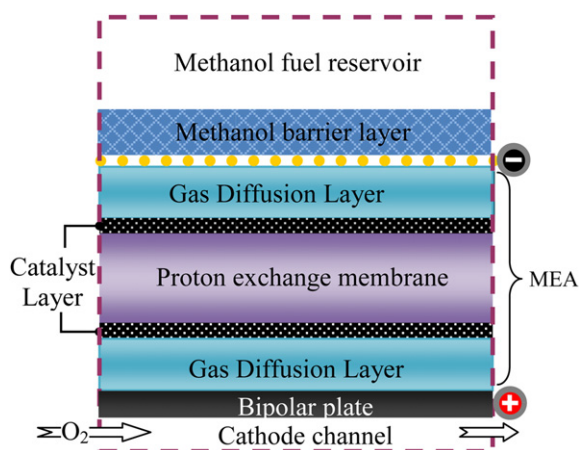 E-mail address: faghri@engr.uconn.edu (A. Faghri).

Fig. 1. Semi-passive DMFC fed with high concentration methanol solutions.

$$6H^+ + 6e^- + 1.5O_2 \rightarrow 3H_2O \qquad (2)$$

The overall reaction is:

$$CH_3OH + 1.5O_2 \rightarrow CO_2 + 2H_2O. \qquad (3)$$

DMFCs are better suited for power-hungry portable devices than PEMFCs fed with hydrogen and oxygen or lithium ion batteries. This is primarily due to the ease of handling and high theoretical energy density of methanol (6.1 kWh kg^{-1}). A DMFC can be categorized as active, semi-passive, or passive based on the fuel and oxidant supply modes. Active DMFCs are fed with methanol solutions and oxidant using pumps, fans, sensors, heaters and humidity components. In an active system, the fuel and oxidant supply rates can be accurately controlled, producing the highest performance. Passive DMFCs use no auxiliary components for the supply of methanol, water and oxygen. The supplies are passively transported from the methanol tank and ambient air to the membrane electrode assembly (MEA) by capillary forces, gravity and concentration gradients. Passive DMFCs are more compact, simple, and reliable, and are thus more suitable for portable and micro/miniature applications requiring low power (<10 W). Semi-passive DMFCs have a passive anode and active cathode or an active anode and passive cathode.

Although DMFCs have advantages over rechargeable batteries, the current power supply systems in portable electrical devices are still mainly dominated by rechargeable lithium and nickel based batteries. The commercialization of DMFCs has been continuously postponed since the early 2000s due to their high cost, low lifetime and technical barriers. Methanol crossover, a phenomena in which methanol diffuses from the anode to the cathode through the membrane, is one of the most notable technical barriers of DMFCs. Methanol crossover is caused by the inherent water transport property of the Nafion® membrane (the most widely used proton exchange membrane) and the miscibility between methanol and water. The crossed-over methanol reacts with oxygen (eq. (3)) at the cathode due to the high overpotential. This reaction (eq. (3)) reduces the cell voltage and decreases the fuel efficiency, since it does not generate electricity. In general, dilute methanol solutions are used as fuel in order to decrease the methanol crossover in DMFCs. Experiments show that the optimized methanol concentration is 1–2 M (3–6 wt%) for active DMFCs and about 3 M (10 wt%) for passive DMFCs [1–5]. Mass transport involving methanol, water, carbon dioxide and oxygen in both active [6–13] and passive [4,5,14–21] DMFCs fed with dilute methanol solutions have been

extensively studied. Table 1 lists the representative studies on mass transport in DMFCs using dilute methanol solutions. Detailed studies on mass transport in DMFCs using dilute methanol solutions have been reviewed [24–29]. Nevertheless, the energy density of the DMFC is significantly decreased by using dilute methanol solution. In order to take advantage of the high energy density of methanol, high concentration methanol solutions should be stored in the anode fuel reservoir for practical applications. In order to prevent severe methanol crossover, the methanol concentration should be diluted to an appropriate level before it reaches the anode CL.

Water management is a challenging aspect, closely related to the methanol crossover in DMFCs fed with high concentration methanol. Water is required in the methanol oxidation reaction, eq. (1). The water to methanol weight ratio in the ACL has to significantly exceed 1:1 in order to sustain the anode reaction or methanol will partially oxidize to form formic acid, methylformate, and formaldehyde [30,31]. These intermediate species may poison the catalyst and deteriorate the fuel cell performance. Secondly, water is required to hydrate the electrolyte membrane because the proton conductive resistance of the Nafion® membrane is inversely proportional to its water content [32]. Unfortunately, little to no water is available from the high concentration methanol solution in the anode fuel reservoir to hydrate the Nafion® membrane.

This review paper emphasizes the fundamental and applied research and prototype designs of DMFCs fed with high concentration methanol in order to solve the aforementioned problems and achieve stable fuel cell performance. In Section 2, the fundamental and applied experimental studies on DMFC single cells will be discussed, including improving the methanol supply, water management, oxygen supply and carbon dioxide release. Section 3 will show the advances of DMFC prototype designs and developments. Section 4 will present several unresolved issues and challenges in the development of both DMFC single cells and stacks fed with high concentration methanol. Modeling and simulation of DMFCs are presented in Part II of the review paper.

2. Fundamental and applied research on DMFC single cells

As shown in eqs. (1)–(3), species including methanol, water, oxygen and carbon dioxide are involved in fuel cell reactions. Studies on the multi-phase transport phenomena and interactions between species in DMFCs are important to improve the fuel cell performance. Investigations of methanol supply, water management, oxygen supply and carbon dioxide release will be discussed in detail in this section.

2.1. Methanol supply

As a key technical issue, methanol crossover has been extensively studied in DMFCs with dilute methanol solutions in the past decade. Methods such as using dilute methanol solutions [4,14], using polytetrafluoroethylene (PTFE) treated anode gas diffusion layers (GDLs) [22] and adding hydrophobic micro porous layers (MPLs) [6,7] can decrease the methanol crossover. In DMFCs using high concentration methanol, however, the methanol concentration in the fuel reservoir is so high that none of these methods can decrease the methanol crossover to an acceptable level. Well-engineered methanol supply systems should be applied to assure low methanol concentration in the anode CL and achieve good performance without severe methanol crossover. The methanol supply system can be improved by active or passive methods. The most recent fundamental studies on DMFC single cells using high concentration methanol are listed in Table 2. The methanol concentration, maximum power density, operating temperature,

Table 1
Recent experimental studies on heat and mass transfer in direct methanol fuel cells using dilute methanol solutions.

Investigator	Methanol concentration	Power density (mW cm^{-2})	T (°C)	An/Ca	Fuel supply techniques	Technologies
Liu et al. [4,14], 2005, 2006	1–5 M	36 (5 M)	RT[a]	P/P[b]	L[c]	The effects of methanol concentration and membrane thickness on the performance, fuel efficiency, and operating temperature of a passive DMFC were investigated. It was found that higher methanol concentration led to an increase in the cell operating temperature. The fuel efficiency determined under constant voltage discharge decreased with the increase in methanol concentration and the increase in membrane thickness.
Lu et al. [6], 2006	2 M	56	60	A/A	L	A micro porous layer (MPL) was utilized at the cathode of the MEA and Nafion 112 was used as electrolyte membrane to promote water back flow. Influences of operating conditions, such as anode and cathode stoichiometry, cell temperature, current density on water transport and overall performance were studied. Results showed that hydrophobic MPL can build up hydraulic pressure on the cathode side and drive water from cathode to anode.
Chu and Jiang [15], 2006	0.1–5 M	38 (3 M, 30 °C)	2–40	P/P	L	The fuel efficiency of a liquid-feed passive DMFC was experimentally studied. The effects of several operating conditions (methanol concentration, discharge voltage, and ambient temperature) on fuel efficiency were analyzed under a constant voltage discharge.
Liu et al. [7], 2006	2, 3 M	60	60	A/A	L	A novel MEA was designed to attain low methanol crossover, low water crossover, and high cell performance simultaneously. A catalyzed diffusion medium was employed as a methanol barrier layer to reduce the methanol crossover, while a highly hydrophobic cathode micro-porous layer was employed to build up the hydraulic pressure at the cathode and hence, drive the product water from the cathode to the anode to lower the total water crossover.
Guo and Faghri [16], 2006	1–5 M	20 (2, 3 M)	RT	P/P	L	Different metal-mesh current-collectors with varying thicknesses were compared. Each current-collector was either put directly onto the anode DL or hot-pressed on the anode DL. It was found that the cell with the thicker current-collector that was hot pressed showed the highest performance as a result of the lowest contact resistance between the anode CC and DL.
Guo and Faghri [17], 2006	1–5 M	11	RT	P/P	L	An air filter with low-thermal conductivity was added at the cathode of a passive DMFC to reduce the heat dissipation from the cathode and increase the cell operating temperature. The added air filter also increased the mass-transfer resistance of water vapor and reduced the liquid water evaporation at the cathode. The added air filter, however, also increased the mass-transfer resistances of oxygen from the ambient air to the cathode CL. Consequently, the oxygen concentration in the cathode CL is decreased and the cathode voltage is lowered.
Xu et al. [22], 2006	1–4 M	NA	75	A/A	L	The in-plane methanol transport depended highly on the thickness of the anode gas diffusion layer (GDL) and its PTFE content. It was found that a thicker GDL could lead to a more uniform methanol distribution over the electrode while increasing the through plane mass transfer resistance. The PTFE treatment of the GDL increased the mass transport resistance of the GDL.
Song et al. [18], 2007	3 M	NA	50, 70	A/A	L	The water crossover behavior in a passive DMFC was investigated by calculating both the water-transport coefficient and methanol efficiency. The mass balance was conducted under a constant current discharge of 120 mA cm^{-2}. It was found that changes in the cathode diffusion layer structure and membrane thickness were effective ways to control the water crossover. They also found that the methanol crossover was lowered with the reduction of water crossover.
Xu and Zhao [8], 2007	1–4 M	110 (2 M, 70 °C)	30, 50, 70	A/A	L	The effects of the properties of GDL, membrane thickness, current density, temperature, methanol concentration and O$_2$ flow rate were investigated. Water crossover was almost unchanged with current density, and hydrophobic cathode GDL and hydrophobic MPL could enhance water back flow and reduce water crossover. The water-crossover flux increased nearly eight times when the temperature was increased from 30 °C to 70 °C due to the increased water diffusivity and the electro-osmotic drag coefficient. In addition, water back flow could be enhanced by using thinner electrolyte membrane.
Jewett et al. [5], 2007	1–5 M	25 (3 M)	RT	P/P	L	An additional GDL was applied at the cathode of the fuel cell to improve water management. It was found that water management was improved with the addition of two additional cathode gas diffusion layers and thicker Nafion membranes exhibited greater water balance coefficients, higher fuel utilization efficiency, and greater energy efficiency.
Xu and Zhao [23], 2007	0.25, 1 M	NA	75	A/A	L	A new flow field was developed to enhance the under-rib convection and achieve a more uniform methanol distribution through the GDL.
Xu et al. [19], 2010	2–4 M	50 (3 M)	RT	P/P	L	The methanol and water crossover in passive DMFCs was accurately measured based on the mass balance of the cell discharged under different current loads. The methanol and water crossover and fuel efficiency were evaluated at different methanol concentrations and different constant current loads. The effect of a hydrophobic cathode water management layer on the methanol and water crossover was also investigated. This work first revealed the effect of temperature rise during the cell discharging on the methanol and water crossover and discussed the inherent correlation between the methanol crossover and water crossover.

[a] Room temperature.
[b] Passive/active.
[c] Vapor/liquid.

fuel supply techniques and key technologies of these DMFCs are listed in the subsequent table.

2.1.1. Use vapor fuels instead of liquid fuels

It has been proved in active systems that the vapor-feed DMFC has relatively low methanol crossover compared to the liquid-feed DMFC [60–65]. A vapor-feed DMFC system can either directly use a mixture of methanol and water vapor as fuel or vaporize liquid methanol solutions to drive the fuel cell. In portable power supply systems, fuels in liquid phase are preferred due to their portability and higher energy density than gas fuels. Consequently, liquid methanol is stored in the fuel reservoir, in passive DMFCs. A vapor-feed fuel cell should efficiently vaporize the liquid methanol by heat or vaporizers. Guo and Faghri [39,40] presented a novel vapor-feed DMFC with a passive thermal-fluids management system. The liquid methanol, wicked from a reservoir, was vaporized at a copper evaporation pad by the waste heat produced by the fuel cell during operation. The vapor-feed DMFC reached a power density of 16.5 mW cm^{-2} at a current density of 60 mA cm^{-2}. A heat source was critical for the effective operation of this fuel cell system. With the help of heat pipes, however, the operational waste heat could provide adequate heat to vaporize the methanol. Alternatively, a vaporizer could be used between the reservoir and MEA to vaporize the liquid fuel. During operation, the liquid fuel cannot directly transport through the vaporizer. It will instead be converted to vapor phase through the vaporizer by adsorption and desorption or by evaporation in the micro flow passages of the vaporizer. Different materials have been used as the vaporizer in vapor-feed DMFCs using high concentration methanol [33,34,43,45,46].

Kim [33] applied a Nafion$^{®}$ 112 membrane as the vaporizer in a passive DMFC fed with pure methanol. The vapor-feed DMFC system was able to run 360 h with a power density of 20–25 mW cm^{-2} at room temperature. The calculated fuel efficiency was 57% and the energy density was 0.145 Wh mL^{-1}. Similarly, Pan [36] and Xu et al. [46] used Nafion$^{®}$ 117 membranes as the vaporizer and barrier layers in passive DMFCs. The passive DMFC fed with pure methanol showed a peak power density of 34 mW cm^{-2} and a fuel efficiency of 62% at room temperature [46]. Eccarius et al. [43] applied a polydimethylsiloxane (PDMS) pervaporation membrane in their passive DMFC, supplied with concentrated methanol solutions ranging from 25 (7.5 M) to 100 wt% (pure methanol). The DMFC showed a peak power density of 24 mW cm^{-2} at 50 °C with a 50 wt% (14.3 M) methanol solution. Ren et al. [45] applied a silicon pervaporation membrane in a passive DMFC with pure methanol. The passive fuel cell achieved a peak power density of 70 mW cm^{-2} at the environmental temperature of 32 °C.

Abdelkareem and Nakagawa [34] used hydrophobic porous carbon plates as the vaporizer, located between the fuel reservoir and the current collector. Their passive fuel cell showed a peak power density of 24 mW cm^{-2} with 16 M methanol solution at room temperature. The subsequent studies [66,67] confirmed that methanol and water were transported through the porous carbon plate and gas layer by vapor phase. The partial pressures of methanol, water, and CO$_2$ were measured in situ by gas chromatograph. The equivalent concentration of the gas mixture in the gas layer was about 5–7 M in the optimum conditions.

In summary, Nafion$^{®}$ membranes and hydrophobic porous materials such as PTFE and carbon plates are widely used as vaporizers in vapor-feed DMFCs. Fuel cells with a vaporizer do not require extra power or external devices to vaporize liquid methanol. The evaporation rate of liquid methanol, however, cannot be easily adjusted by the vaporizer. Other components, such as methanol barrier layers [43,46] or methods, such as decreasing the open ratio of the vaporizer [33] (discussed further in following sections) should be applied together with vaporizers to obtain the desired transport rate of methanol vapor. The continuous swelling of the Nafion$^{®}$ membrane caused by methanol, however, will decrease the mechanical strength and cause cracks in the vaporizer. Cheap and strong vaporizers should be developed for long term applications.

2.1.2. Increase the methanol transfer resistance between the reservoir and MEA

Investigations on DMFCs fed with high concentration methanol specifically designed the flow channels [49,53] and current collectors [57] in order to decrease the methanol crossover. The new flow channels and current collectors typically have low open ratios so that the methanol flow rate from the reservoir to the MEA is decreased. The methanol crossover could also be decreased by adopting a methanol barrier layer between the fuel reservoir and the MEA to passively increase the methanol transport resistance, shown in Fig. 1. The methanol barrier layer is usually composed of porous materials with different permeability, determined by physical properties such as porosity, tortuosity and micro pore distribution. Various materials have been used as the methanol barrier layer in the previous studies. This passive method does not need auxiliary devices such as pumps and sensors, which makes it more suitable for single cell or small cell stacks.

Abdelkareem and Nakagawa [34] employed a hydrophobic porous carbon plate and a 2 mm gap between the fuel reservoir and the MEA as a methanol barrier layer and significantly reduced methanol crossover. Kim et al. [35] added hydrogels to the fuel reservoir to reduce methanol crossover of a liquid-feed passive DMFC. By using the hydrogels, the peak power density of the fuel cell was 21.5 mW cm^{-2} with 8 M methanol. Guo and Faghri [17,37] inserted a water storage media between the methanol storage media and the MEA of a passive DMFC. Pure methanol and water were separately delivered to the methanol storage media and water storage media by wicking materials. The water storage media diluted the pure methanol and acted as a methanol barrier layer. The proposed fuel cell successfully ran with pure methanol and drove for 72 h at room temperature, with a power density of 12 mW cm^{-2}. Zhang and Hsing [38] adopted a flexible graphite plate between the flow channel and the MEA in an active liquid-feed DMFC. The newly designed DMFC performed better than conventional DMFCs, using methanol concentrations ranging from 8 M to 20 M at 70 °C. The new DMFC achieved a power density of 22.5 mW cm^{-2} with 12 M methanol.

Several studies investigated the effect of methanol barrier layer properties such as thickness [47,48] and micro pore size [68] on the performance of vapor-feed DMFCs. Results in Fig. 2 indicate that a thicker methanol barrier layer could significantly decrease the methanol crossover, increase the fuel efficiency, and improve the cell performance. Similar conclusions made by He et al. [58] and Abdelkareem et al. [68] state that the anode methanol barrier layer can be used to carefully adjust the methanol transport rate to the anode CL.

As discussed above, methanol barrier layers can effectively decrease the methanol crossover in both vapor-feed and liquid-feed DMFCs fed with high concentration methanol. In general, methanol barrier layers are hydrophobic porous materials with specific thickness, pore size and permeability. Unfortunately, these methanol barrier layers are typically much thicker than the MEA and increase both the weight and volume of the fuel cell. Thin methanol barrier layers with large mass transfer resistance to both liquid and vapor should be developed for compact fuel cells with strict weight and volume restrictions. Similar to the adoption of methanol barrier layers, the MEA could be modified by hydrophobic MPLs to dramatically decrease the methanol crossover

Table 2
Experimental studies on direct methanol fuel cells with emphasis in high concentration methanol solutions.

Investigator	Methanol concentration	Power density (mW cm^{-2})	T (°C)	An/Ca	Fuel supply techniques	Technologies
Kim [33], 2006	Pure	20–25	RT	P/P	V	Liquid methanol was absorbed in the fuel chamber by a porous pulp and was vaporized by a Nafion® 112 membrane. A hydrophobic porous Teflon barrier layer and a fired alumina buffer layer were added at the anode to restrict the diffusion rate of the methanol vapor.
Abdelkareem and Nakagawa [34], 2006	1 M to pure	24 (16 M)	RT	P/P	V	A hydrophobic porous carbon plate was employed between the fuel reservoir and anode current collector.
Kim [35], 2006	4, 8 M	21.5 (8 M)	RT	P/P	L	Hydrogels were added to the fuel reservoir to reduce the rate of methanol crossover
Pan [36], 2006	4 M to pure	50 (10 M)	50	P/P	V	Four Nafion® 117 membranes were stacked as the vaporizer and methanol barrier layers to decrease methanol crossover
Guo and Faghri [17,37], 2006, 2010	Pure	12	RT	P/P	L	A pure methanol storage media and a water storage media were adopted separately. Porous PTFE was used as the air filter to improve the water management.
Zhang and Hsing [38], 2007	8–20 M	22.5 (12 M)	70	A/A	L	An anode plate made of flexible graphite material was used to decrease the methanol crossover. The fuel cell was tested at 70 °C with a supply of 0.8 mL min^{-1} methanol solution and 0.35 L min^{-1} O$_2$ humidified at 65 °C. The high-mass-transfer resistance through the DMFC plate allowed the DMFC to be operated with 12 M methanol at a current density of 150 mA cm^{-2} for 1.5 h.
Guo and Faghri [39,40], 2007, 2009	Pure	16.5	RT	P/P	V	Pure methanol was wicked from a reservoir to a porous evaporation pad where methanol was vaporized.
Abdelkareem and Nakagawa [41], 2007	16 M		RT	P/A	V	A hydrophobic porous carbon plate was employed between the fuel reservoir and anode current collector.
Chan et al. [42], 2008	4, 12 M	(12 M)	RT	P/P	L	The methanol solution stored in the fuel tank was driven by the exhausted CO$_2$ to the anode reaction chamber in response to the methanol consumption rate.
Eccarius et al. [43], 2008	25–100%/ 7.5–24.7 M	24 (50 wt%/14.3 M)	50	P/P	V	The methanol vapor was generated by a polydimethylsiloxane (PDMS) pervaporation membrane and the evaporation rate of methanol into the vapor chamber was controlled by different open area ratios of a solid plate attached to the PDMS membrane.
Eccarius et al. [44], 2008	25–100%/ 7.5–24.7 M	10 (100%/24.7 M)	50	P/P P/A	V	The cathode loss was higher with an air-breathing cathode than with a forced air flow at the cathode because of the lower availability of oxygen. The anode loss was lower with an air-breathing cathode, however, because more water was available for back diffusion from the cathode to the anode. In a high current density range, the overall performance could be better with an air-breathing cathode.
Ren et al. [45], 2009	Pure	40.5 (25 °C, 15% R.H.) 70 (32 °C, 20% R.H.)	25/32	P/P	V	Pure methanol was stored in the anode tank and was vaporized by the pervaporation membrane (silicone membrane). The cathode structure was optimized to maneuver the water supply from the cathode to the anode by back diffusion and back convection.
Xu et al. [46], 2010	6 M to pure	34 (pure)	RT	P/P	V	A Nafion® 117 membrane was used as the pervaporate membrane and different hydrophobic water management layers were used in the cathode to improve the water management.
Li et al. [47], 2010	4 M to pure	75.9 (16 M)	70	P/A	V	A porous PTFE plate was used as a methanol barrier layer, and the relative humidity of the cathode oxygen was 100%.
Li et al. [48], 2010	6 M to pure	116 (20 M)	70	P/A	V	A porous PTFE plate was used as methanol barrier layer and a thinner electrolyte membrane could improve the cell performance.
Wu et al. [49], 2010	2–20 M	21.8 (18 M)	RT	P/P	L	A microfluidic-structured anode flow field plural micro flow passages to create an extremely large interfacial mass-transfer resistance of methanol.
Wu et al. [50], 2010	Pure	19.6	RT	P/P	L	Water retention layers, a thin layer that consisted of nanosized SiO$_2$ particles and Nafion® ionomer, were adopted in the fuel cell to increase the water concentration level of the electrolyte membrane. The MEA with water retention layers on both the anode and the cathode with SiO$_2$ loadings of 0.1 mg cm^{-2} yielded a maximum power density of 19.6 mW cm^{-2}, which is 26% higher than that of the MEA without SiO$_2$ layers.
Wu et al. [51], 2010	Pure	16	RT	P/P	V	The best cell performance was achieved with a 30% PTFE content in the BL (in the range of 0–30%), 30% PTFE content in the MPL (in the range of 0–40%), and 4 mg cm^{-2} carbon loading in the MPL (in the range of 0–6 mg cm^{-2}).

Table 2 (continued)

Investigator	Methanol concentration	Power density (mW cm^{-2})	T (°C)	An/Ca	Fuel supply techniques	Technologies
Masdar et al. [52], 2010	16 M and pure	16 (pure methanol and 0.2 V)	30	P/P	V	A hydrophobic air filter (HAF) with higher hydrophobicity and higher flow resistance increased the water back flow and the current density. The HAF fixation by providing a space from the cathode surface was more effective than that of the direct placement on the cathode surface.
Wang et al. [53], 2011	1–8 M	12.5 (7 M)	RT	P/P	L	An anode flow field composed of the parallel flow field and the perforated flow field structure was designed. The new flow field can enhance the methanol transfer resistance from the flow field to the anode diffusion layer. The results showed that the micro DMFC with an anode open ratio of 40% and a thickness of 300 μm had the optimal performance, 12.5 mW cm^{-2}, using 7 M methanol solution.
Wu et al. [54], 2011	Pure	70 (60 °C)	30, 45, 60	A/A	V	The design parameters of the MEA have been studied and a net water transport from the cathode to the anode was observed with well designed MEAs. The results showed that thinning the anode GDL and the membrane as well as thickening the cathode GDL can enhance the water transport flux from the cathode to the anode.
Park et al. [55], 2012	50–95 vol%	35.1 (95 vol% methanol)	RT	P/P	L	An MEA with multilayer electrodes was developed, including a barrier layer to limit the crossover of high concentration methanol, a hydrophobic layer to reduce water crossover, and a hydrophilic layer to enhance the water recovery from the cathode to the anode.
Kang et al. [56], 2012	1–8 M	78 (8 M)	60	A/A	L	A hydrophobic anode MPL was adopted to decrease the methanol crossover.
Yuan et al. [57], 2012	0.5–8 M	3.5 (8 M)	RT	P/P	L	The anode current collector with a circular-hole-array pattern and certain open ratios were developed to decrease the methanol crossover.
He et al. [58], 2012	8 M, 16 M, pure	18 (pure)	RT	P/P	L	The influences of the anode methanol barrier layer and the cathode water management layer have been investigated. It was indicated that the anode methanol barrier layer can adjust the methanol transport rate to the anode CL and the cathode water management layer could decrease the water loss to the ambient and enhance the water back flow. The optimum cell performance was achieved with a relatively thick methanol barrier layer, 1.5 mm, and a thick water management layer, 1.9 mm, when the DMFC is operated with pure methanol.
Wu et al. [59], 2012	Pure	NA	RT	A/A	V	The effect of the water concentration in the anode CL on the product distribution of the methanol oxidation reaction, the anode potential, and the cell internal resistance in a DMFC operating with pure methanol have been studied. It was observed that the main product of the anode MOR was still carbon dioxide even when the water concentration in the anode CL is extremely low.

[55,56]. Compared to the methanol barrier layer, MPLs are much thinner and will not significantly increase the weight and volume of the fuel cell.

2.2. Water management

In order to increase the energy density of the fuel cell, neither water nor dilute methanol should be added to the fuel reservoir. The lack of water from the methanol solution makes the water management in DMFCs fed with high concentration methanol more difficult. Studies on water management indicated that it is extremely important to simultaneously hydrate the electrolyte membrane and dilute the methanol in DMFCs fed with high concentration methanol. The insufficient supply of water to the electrolyte membrane significantly decreased the cell performance [47,56,69] due to the decrease in Nafion® conductivity and slow methanol oxidation reaction (eq. (1)). Studies on the effect of oxygen's relative humidity on water management, as shown in Fig. 3, indicated that the performance of the semi-passive DMFC significantly decreased with decreasing relative humidity. The peak power density decreased from 60.6 to 34.6 and to 25.0 mW cm^{-2} and the internal resistance increased correspondingly when the

relative humidity of the oxygen decreased from 100% to 39.6% and to 13.9%.

According to eqs. (1)–(3), water is consumed at the anode and generated at the cathode: 1/6 water molecules and 1/6 methanol molecules are consumed to generate one electron and one proton at the anode side, while 1/2 water molecules are generated when one electron and one proton are consumed at the cathode side. The overall generated water is more than the consumed water, which makes recycling the water within the fuel cell possible. In order to improve water management, water generated from the cathode reaction should be recycled, either externally or internally, to the anode. To recycle the cathode water externally, the water generated in the cathode reaction is collected using fans, liquid/gas separators, and condensers. The collected water is recycled to the anode with the help of auxiliary devices such as pumps, tubes, methanol sensors and mixing chambers, so the high concentration methanol is diluted before it reaches the MEA. The active method can accurately control the methanol concentration and its flow rate, making this method more suitable for large fuel cell stack applications. For instance, Bostaph and Marshall [70] and Xie et al. [71] developed a water recovery and recirculation system for a 2 W DMFC stack. The active water recovery system recycled water in the methanol/water mixture expelled from the anode and the water expelled
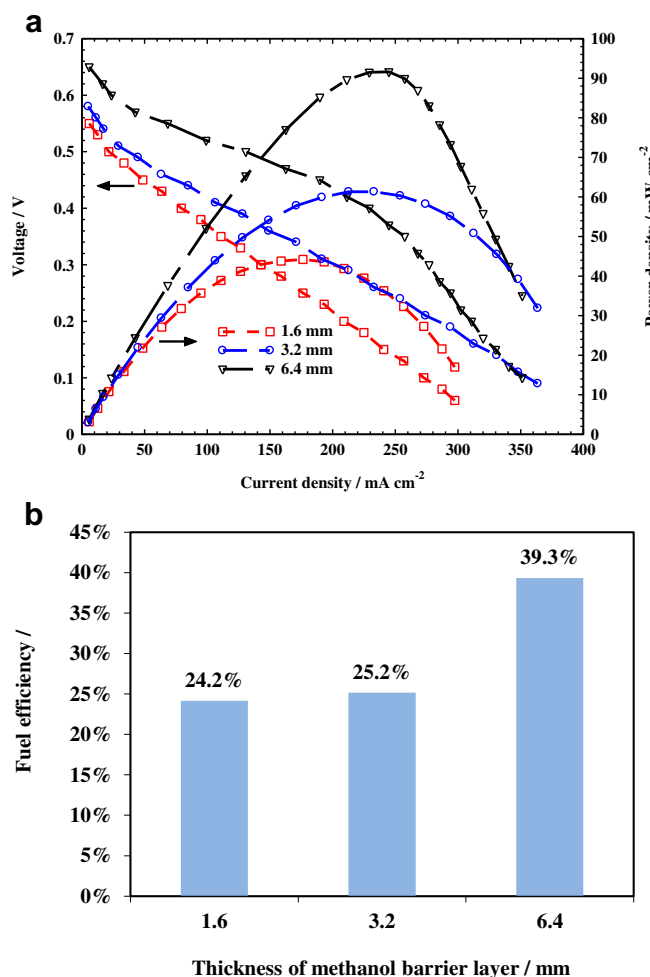
Fig. 2. (a) Performances and (b) fuel efficiency of a DMFC with different methanol barrier layers (Nafion® 117 membrane, 70 °C temperature, 16 M methanol, 100 mL min^{-1} oxygen, and 100% cathode relative humidity, fuel efficiency was measured at 200 mA cm^{-2} discharging current density). Figure adopted from [48].

Fig. 3. Effect of the cathode relative humidity on the performance of the cell: (a) current–voltage and current–power density; (b) current-resistance (16 M methanol solution, 70 °C cell temperature, 100 mL min^{-1} oxygen flow rate, and 1.0 atm cathode pressure). Figure adopted from [47].

from the cathode with the help of liquid pumps, fans, a liquid/gas separation system, and tubes. The recycled water, together with deionized (DI) water from a water tank, diluted the pure methanol from the methanol tank to approximately 4 vol% before the fuel was fed to the stack with a methanol concentration sensor and a series of liquid pumps.

The cathode water can also be internally pushed back to the anode with the help of a concentration gradient and hydraulic pressure gradient of water between the anode and cathode [8]. The internal water recycling method does not need auxiliary devices such as pumps and fans, which makes it more suitable for single cells and small stacks. The key to passive water management in DMFCs using high concentration methanol is to decrease the water loss from the cathode and enhance the water back flow from the cathode to the anode. The water loss can be decreased by adding hydrophobic water management layers to the cathode, which increase the water transfer resistance.

Guo and Faghri [17,37] improved the water management of a pure-methanol-feed DMFC using different electrolyte membranes and air filters. By using an air filter made of porous PTFE sheets with a 25 µm pore size and a 1.6 mm thickness, a water neutral condition was achieved, meaning no extra supply of water was required during operation. Eccarius et al. [43] studied the effect of the cathode water supply in a vapor-feed DMFC by actively injecting
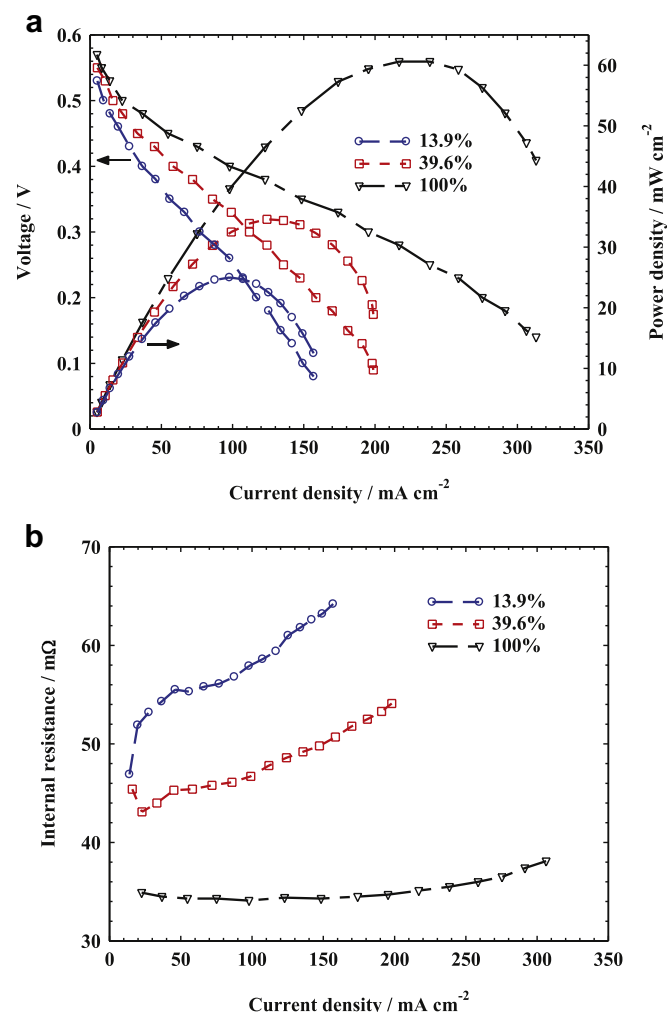
0.25 mL of water to the cathode side of the fuel cell. Different types of gas diffusion layers were also used to compare their effects on the water management system. Masdar et al. [52], Xu et al. [72] and He at al. [58] studied the effects of hydrophobic air filters at the cathode on the water transport of vapor-feed DMFCs. The hydrophobic air filter with a higher hydrophobicity and higher flow resistance was found to improve the water management.

The water back flow from the cathode to the anode could be enhanced by improving the MEA structure and properties. Wu et al. [50] developed an MEA with water retention layers consisting of nanosized SiO$_2$ particles and Nafion® ionomer on both sides of the electrolyte membrane. This water retention layer enhanced the water retention and hydrated the Nafion® membrane. The DMFC was tested with pure methanol at room temperatures of 23.8–24.6 °C and relative humidities of 63–75%. Their results showed that the MEA with water retention layers on both the anode and the cathode with SiO$_2$ loadings of 0.1 mg cm^{-2} yielded a maximum power density of 19.6 mW cm^{-2}. This result was 26% higher than that of the MEA without SiO$_2$ layers. The improved cell performance was mainly attributed to the increased cathode and anode water concentration level by adding water retention layers. Wu et al. [51,54] also studied the effects of the MEA components on the water transport. A net water transport from the cathode to the

anode was observed with well designed MEAs. The results showed that thinning the anode GDL and the membrane and thickening the cathode GDL can enhance the water transport flux from the cathode to the anode. Li et al. [48] studied the effect of electrolyte membrane thickness on cell performance and water management using a semi-passive DMFC operating at 70 °C with 16 M liquid methanol. The water crossover coefficient is defined as the number of water molecules transported from the anode to the cathode combined with the generation of one electron molecule. It is shown in Fig. 4 that the water crossover coefficient decreased from positive to negative when a thinner electrolyte membrane was employed. At the same time, the peak power density sharply increased from 48.3 to 61.0 and then to 114.3 mW cm^{-2} with Nafion® 117, 115, and 212 membranes, respectively.

As shown in Fig. 5, the water management of the fuel cell has been significantly improved since adding water management and air filter layers and improving the MEA structure. The passive vapor-feed DMFC fed with pure methanol showed a peak power density of 34 mW cm^{-2} and a fuel efficiency of 72% at room temperature. However, the water management layers are typically thicker than the MEA and increase the overall weight and volume of the fuel cell. Alternatively, the simple analysis conducted by Li and Faghri [73] indicated that mass transfer resistance can be increased without increasing the weight and volume of the fuel cell by adopting perforated layers with different open ratios. The performance, tested with cathode open ratios varying from 7% to 38%, shown in Fig. 6(a), indicated that with an anode open ratio of
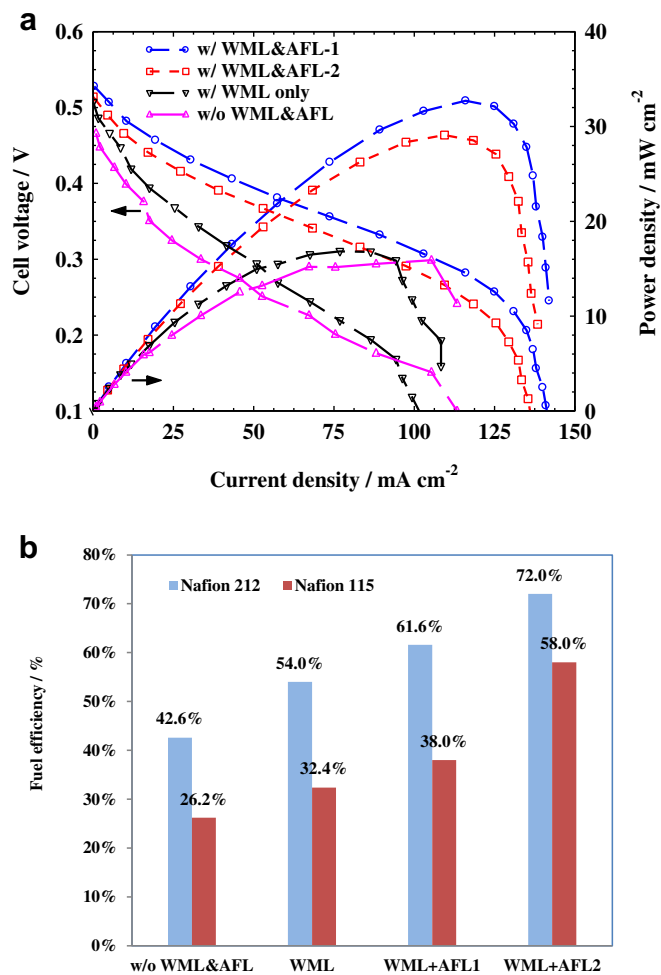

Fig. 4. (a) Performances and (b) water crossover coefficient of a DMFC with different electrolyte membranes (70 °C temperature, 16 M methanol, 100 mL min^{-1} oxygen, and 100% cathode relative humidity. The crossover coefficients were measured at 200 mA cm^{-2} discharging current density). Figure adopted from [48].

Fig. 5. (a) Cell performances and (b) fuel efficiencies of a vapor-feed DMFC passively fed with pure methanol with different water management layers and air filter layers. Figure adopted from [71].

12%, the cell performance showed a peak value at the cathode open ratio of 20% in a passive DMFC fed with pure methanol due to the improved water management. The fuel efficiencies, as shown in Fig. 6(b), indicated that the fuel efficiency was the highest, 78.3%, with a cathode open ratio around 12%. Water management is also coupled with oxygen supply. If the mass transfer resistance increases too much after using very thick water management layers [51,58] or a very low cathode open ratio [73], the oxygen supply could be insufficient and thus deteriorate the fuel cell performance. Details regarding oxygen supply will be discussed further in the following section.

2.3. Oxygen supply

In a conventional DMFC fed with dilute methanol, the transport of oxygen from the ambient air to the reaction sites may be impeded by cathode water flooding. The water flooding is caused by the accumulation of water crossed-over from the anode and water generated in the cathode reaction (eq. (2)). In a DMFC fed with high concentration methanol, however, the water management layer prevents the water flooding thereby not affecting the transport of oxygen. Furthermore, studies on the effect of oxygen transport modes in semi-passive and active DMFCs using high concentration methanol solutions showed that cell performances were not restricted by limited oxygen transport [41,44,47,59].
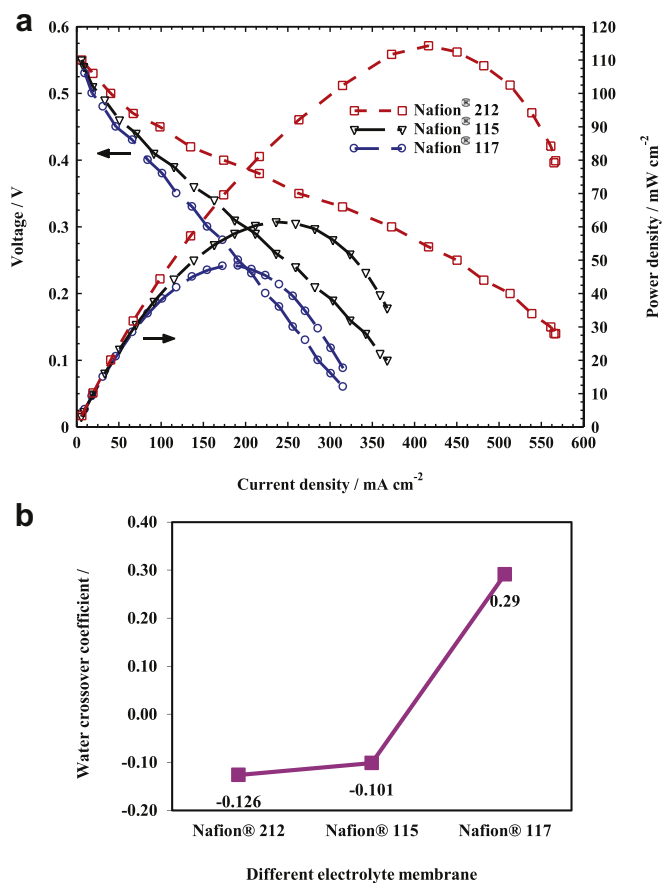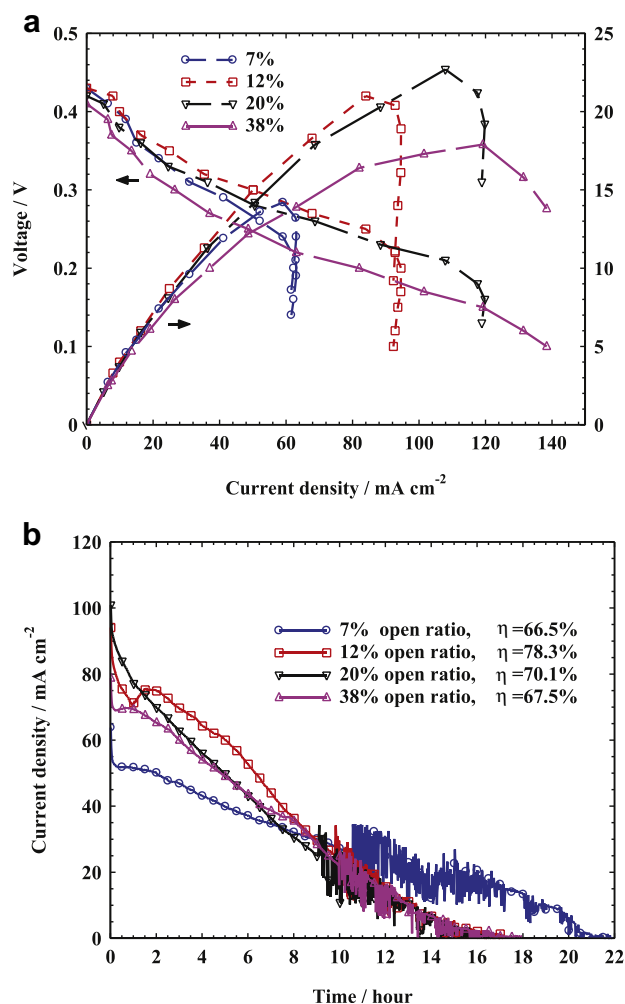
Fig. 6. Performance of a DMFC operated at room temperature with pure methanol, an anode open ratio of 12%, and various cathode open ratios (7%, 12%, 20%, 38%) represented by (a) current density vs. voltage and power density and (b) variations in current density with time during discharge at 0.2 V with 2 mL methanol. Figure adopted from [72].

Fig. 7. (a) Cell performances and (b) water crossover coefficients of a DMFC passively fed with high concentration methanol solution and various oxygen flow rates (16 M methanol solution, 70 °C cell temperature, 100% cathode relative humidity, 1.0 atm cathode pressure). Figure adopted from [47].

Li et al. [47] studied the effect of oxygen flow rates on a semi-passive DMFC fed with 16 M methanol solution. The oxygen flow rates at the cathode varied from 50 to 1000 mL min^{-1} and the relative humidity was set to 100%. Results in Fig. 7 show that the cell performance was improved by decreasing the oxygen flow rate. Water in the cathode could not evaporate because the cathode relative humidity was set at 100%. Only liquid water can be removed by the oxygen flow. The limiting current density did not increase with an increased oxygen flow rate, indicating that oxygen was not severely blocked by water droplets in the cathode channel. On the contrary, the cell performance decreased and the water crossover coefficient increased with an increased oxygen flow rate because less water flowed back from the cathode to the anode. In a related study, Abdelkareem and Nakagawa [41] investigated the effects of passive and active supplies (0.1 and 1 L min^{-1}) of oxygen on a DMFC using 16 M methanol solution at room temperature. Lower oxygen flow rates to the cathode also led to a better cell performance because high oxygen flow rates may lower the operating temperature of the fuel cell. The best cell performance was achieved at the air breathing condition. The improved performance with a decreased oxygen flow rate could be attributed to the
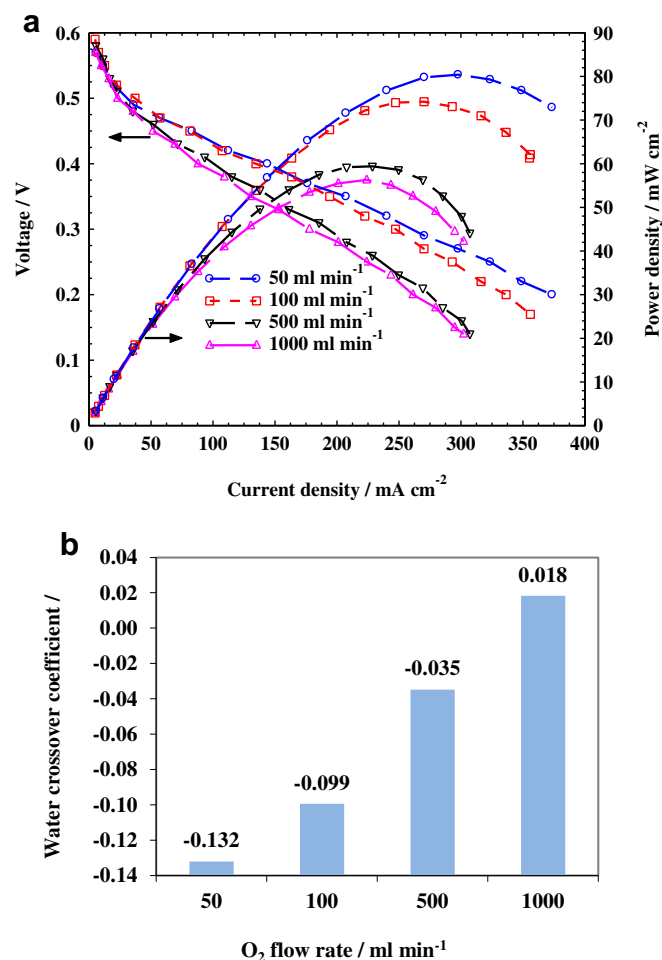
reduction in the internal resistance and the anode potential because of an increased water concentration in the anode CL [59].

Detailed investigations of oxygen transfer indicated that the oxygen supply had different effects on the anode and cathode overpotential of the fuel cell. Studies by Eccarius et al. [44] indicated that the cathode voltage loss was higher with an air-breathing cathode than with a forced air flow as a result of lower oxygen availability. The anode voltage loss was lower with an air-breathing cathode, however, as more water was available for back diffusion from the cathode to the anode. In a high current density range, the overall performance could be improved by using an air-breathing cathode.

The above research showed that even under the passive supply mode in a DMFC fed with pure methanol, the oxygen supply is sufficient. Xu et al. [46] and Masdar [52] indicated that the oxygen supply is still sufficient in passive DMFCs fed with pure methanol even after adding two water management layers at the cathode. Further increasing the mass transfer resistance at the cathode may result in deteriorated cell performance due to the limited oxygen supply [73].

2.4. Carbon dioxide release

According to the anode reaction in eq. (1), methanol and water are consumed and carbon dioxide is generated during the cell

operation. The release of carbon dioxide from the MEA interacts with the transport of methanol and water to the MEA, but the gas and liquid flow in opposite directions [74,75]. The produced CO_2 flows from the MEA to the reservoir and the liquid methanol and water flow from the reservoir to the MEA. Consequently, a proper management of carbon dioxide removal helps to improve the methanol and water management in DMFCs using high concentration methanol.

Chan et al. [42] proposed a self-regulated passive DMFC using high concentration methanol solutions. During operation, the methanol solution stored in the fuel tank was driven by the exhausted carbon dioxide to the anode reaction chamber in response to the methanol consumption rate. The passive DMFC with the fuel feeding system and 12 M methanol solution yielded a stable performance and showed nearly identical cell performance to that of a conventional passive fuel cell with 4 M methanol solution. The self-regulated fuel cell supplied with 12 M methanol solution could successfully operate at a current density of 30 mA cm^{-2} for 14.5 h.

The effects of a CO_2 gas layer [68] and a gas mixing layer [73], gaps formed between the MEA and the methanol barrier layer, have been studied. It was found that the CO_2 gas layer was one of the most important factors in limiting methanol transport. The resistance of the CO_2 gas layer was higher at current densities exceeding 60 mA cm^{-2}, and the resistivity gradually increased with an increasing gas layer thickness from 1 to 2, 3, and 7 mm. Furthermore, the resistivity of the CO_2 gas layer was also related to the properties of methanol barrier layers such as permeability and thickness.

DMFCs fed with high concentration methanol use methanol vaporizers, methanol barrier layers, and water management layers. These DMFCs have high mass transfer resistances of CO_2 and complicate the CO_2 transfer. Unfortunately, the CO_2 transfer in the fuel cell using high concentration methanol is not fully understood. Further studies on the pressure of CO_2 in fuel cells and the CO_2 crossover rate through the Nafion® membrane should be conducted.

2.5. Summary of improvements on passive DMFC design

Mass management is critical in DMFCs using high concentration methanol in order to achieve low methanol crossover, full hydration of the Nafion® membrane, and the water neutral condition. The interactions between the methanol, water, CO_2 and O_2, coupled with the phase change phenomena, complicate the mass management and fuel cell design. For a completely passive DMFC system, the following principles (shown in Fig. 8) are suggested to improve the mass management and enhance the fuel cell performance:

1) Increasing the anode mass transfer resistance between the fuel reservoir and the anode current collector to decrease the methanol crossover;
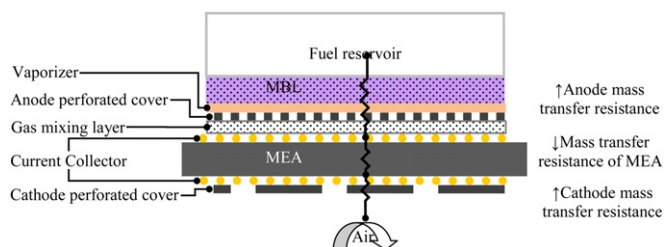

Fig. 8. Principals of the structure optimization of a DMFC fed with high concentration methanol solutions including pure methanol.

2) Decreasing the mass transfer resistance of the electrolyte membrane to increase the water back flow;
3) Increasing the cathode mass transfer resistance between the cathode current collector and the ambient air to decrease the water loss.

3. Advances in DMFC prototype designs and developments

Restricted by the principles of thermodynamics, the theoretical open circuit potential of a DMFC is about 1.21 V [76–78]. The practical working voltage of a DMFC, however, is usually lower than 0.5 V due to the methanol crossover. The voltage required to power portable devices is at least 1.5 V. As a result, fuel cells should be connected in series (as a stack) to provide enough voltage and power. The uniform distributions of fuel and oxidant throughout the fuel cell are challenging when the effective area of the MEA is very large, however. The fuel and oxidant supply can be easily improved in a fuel cell stack with several smaller cells connected in parallel. Consequently, studies on fuel cell stacks with single cells connected in series and/or parallel are required for practical applications.

3.1. DMFC stacks using dilute methanol solutions

3.1.1. Active DMFC stacks

Due to the inherent methanol crossover, most DMFC stacks used dilute methanol as fuels [25,26,79]. Active stacks use auxiliary devices such as fans, pumps, sensors and tubes to accurately control the flow rates and concentrations of the fuel and oxidants. They are usually used in applications requiring relatively high power (>10 W).

Ren et al. [80] developed a five-cell stack with active supplies of 1 M methanol and air at 30 psi. Each cell had an active area of 45 cm^2 and the total volume of the stack was 45 cm^3. The stack could continuously generate 17 W power and 300 W L^{-1} at 60 °C for portable applications and 50 W and 1 kW L^{-1} at approximately 100 °C for transportation applications. The fuel efficiency of the stack was higher than 90% at 0.45 V with 0.5 M methanol and about 82% with 1 M methanol.

Dohle et al. [81] developed a 71-cell DMFC stack with an active area of 144 cm^2 for each cell. The weight of the stack was 12 kg and the dimensions of the stack are 16 × 16 × 16.5 cm^3. The auxiliary components, including a water/methanol tank, a heat exchanger, a pump, and compressors, were driven by the DMFC stack itself without external power sources. The effects of the Nafion® content in the catalyst layer in a range of 5–16 wt% were investigated. The best performance was achieved when the Nafion® content was 7 wt %. Stainless steel and gold-plated stainless steel were used as current collectors, revealing that gold-plating reduced the ohmic resistance by orders of two. The fuel cell stack achieved a power density of 30.4 mW cm^{-2} at 64 °C with 1 M methanol solution and air under ambient pressure. The stoichiometric air flow rate was 2–3. The power density of the stack was increased by raising cathode pressure or by using pure oxygen. The maximum power density increased from 100 mW cm^{-2} using air to 150 mW cm^{-2} using oxygen at 3 bar absolute pressure with 1 M methanol solution at 80 °C.

In 2000, Ha et al. [82] developed a 10 W DMFC stack composed of six single cells with a 52 cm^2 electrode area. The stack had a graphite bipolar plate and operated with 2.5 M methanol at a flow rate of 300 mL min^{-1} under 25–50 °C. The maximum power densities were 6.3 W (121 mW cm^{-2}) at 87 mA cm^{-2} and 25 °C and 10.8 W (207 mW cm^{-2}) at 99 mA cm^{-2} and 50 °C. Nafion® 115 and Nafion® 117 membranes were used in the MEAs.

Oedegaard and Hentschel [83] developed a DMFC stack consisting of twelve cells with a 7×7 cm^2 active area for each cell. The peak power of the stack was 30 W (50 mW cm^{-2}) with 1 M methanol solution supplied at 60 mL min^{-1} and air supplied at 4.7 L min^{-1} at 60 °C. The effect of methanol concentration on the stack performance showed that the 1 M test achieved the best performance. The stack produced a maximum efficiency of about 25% at a current density of 125 mA cm^{-2}.

3.1.2. Passive and semi-passive DMFC stacks

Passive and semi-passive DMFC stacks use few or no auxiliary devices during operation. They are more compact and reliable than the active stacks and thus more suitable for portable devices. Investigations on passive and semi-passive DMFC stacks [16,20,84–94] are listed in Table 3. The methanol concentration, active area of the MEAs, power (or power density), fuel supply modes, and key technologies of these stacks are summarized in Table 3.

In all of the active and passive DMFC stacks listed in Table 3, the optimal methanol concentration was dependent on the design of the MEA and stack configuration. However, the optimized methanol concentrations were not higher than 5 M in most of the studies. Both the stack performance and the fuel efficiency decreased with an increased methanol concentration due to methanol crossover, especially when the methanol concentration was higher than 5 M. The application of dilute methanol solutions significantly sacrificed the energy density of the DMFC stack. In order to increase the energy density of the DMFC stack, high concentration methanol should be fed to the fuel tank.

3.2. DMFC stack development using high concentration methanol

Techniques used in the DMFC single cell fed with high concentration methanol, such as improving the fuel-feed system, water management, oxygen supply, and carbon dioxide release should be adopted in the stack or prototype design. The fuel cell prototypes using high concentration methanol, including pure methanol, have attracted more attention in recent years. Table 4 lists the fuel and air supply modes, year, methanol concentration, power or power density, and the main features of the latest DMFC prototypes and products.

Faghri and Guo [104] designed a vapor feed, bi-cell stack using a passive fuel delivery system and a passive water management system, shown in Fig. 9. Pure methanol and water transport separately from the methanol and water tanks with the assistance of wicking materials and are vaporized by an electric heater in the fuel chamber. The stack operated for 400 h at 22 mA cm^{-2} and room temperature.

Tsujiguchi et al. [115] designed and developed a vertically oriented passive DMFC stack consisting of eight single cells, with a 1.5×5.5 cm^2 active area per cell. A porous carbon plate was used as the vaporizer and a CO_2 gas layer was used as a methanol barrier layer to decrease the methanol crossover and improve the water management. Methanol concentrations varying from 70 wt% to 100 wt% were tested and the power densities increased with the increasing methanol concentration (20 mW cm^{-2} for 70 wt%, 25 mW cm^{-2} for 80 wt%, and 30 mW cm^{-2} for 90 and 100 wt%). Power generation continued for 85 h until the 12 cm^3 pure methanol was completely consumed. The volumetric energy density was calculated to be approximately 800 Wh L^{-1}. The maximum power output of 1.8 W was obtained with 100% methanol for the DMFC stack. A non-uniform cell voltage among the eight unit cells was found, which explained the relationship between decreasing power output and increasing current.

Besides the fundamental research conducted in universities and research institutes, many companies have been active in the design and development of portable DMFC prototypes and products due to the huge potential markets for the portable power supplies [118].

Manhattan Scientific Inc., together with Energy Related Devices Inc. (ERD) [97], developed fuel cells (Micro Fuel Cell) for portable electronic applications in 2001. A Micro Fuel Cell was reported to have achieved a specific energy density of 400 Wh kg^{-1} with test cells running passively at ambient conditions on methanol fuel. The Micro Fuel Cell achieved a specific energy output more than three times greater than standard lithium ion batteries used for cellular telephones, and it ran a cellular phone on standby for 69 h over a two-week period with less than one ounce of methanol fuel. No loss of peak power performance was observed.

Motorola [95,96] developed a semi-passive DMFC stack that works at room temperature. Pure methanol and DI water were stored in the methanol and water tanks separately. Methanol was diluted by pumps and methanol sensors to 1 M methanol and delivered to the MEA, while air was breathed from the ambient. The stack, consisting of four MEAs with an active area of 2×2 cm^2 each and a total volume of 166 cm^3, could generate a net power output of 100 mW. The peak power density of a single MEA was 30–35 mW cm^{-2}. The ancillary system components, including pumps, methanol concentration controls, DC/DC converter, and battery management, consumed 50% of the gross power output from the fuel cell. In a demonstration, the 100 mW fuel cell system powered a PDA for a whole week with a resistive load of 100 Ω.

Motorola Labs [70,71] also developed a 1–2 W active DMFC prototype using pure methanol and DI water stored in separate tanks as the fuel. The air was actively supplied by electric fans. A water recovery and recirculation system was proposed to recycle water from the methanol/water mixture expelled from the anode and the water expelled from the cathode. The recycled water, together with the DI water from the tank, diluted the methanol to approximately 1 M before the fuel was fed to the MEAs. The prototype, using bipolar graphite stacks with six cells and with a total active area of 110 cm^2, achieved 2 W net output, or 20 mW cm^{-2}, at approximately 3 V, or 0.5 V per cell. The air flow rate was approximately 320 mL min^{-1} and the diluted fuel (1 M) flow rate was approximately 100 mL h^{-1}. The stack temperature was able to reach 50–60 °C under normal operation conditions. The assembled stack had a total volume of 86.7 cm^3 and a weight of 180 g. The calculated specific power and power density of this stack were 37 W kg^{-1} and 77 W L^{-1}, respectively.

In June 2004, Toshiba [98] demonstrated the world's smallest DMFC with 100 mW output, featuring fuel cell dimensions of $22 \times 56 \times 4.5$ mm^3 and a weight of 8.5 g. In 2005, Toshiba [103] unveiled two DMFC prototypes; one generated 100 mW of power, the other generated 300 mW, and both were integrated into MP3 players. The fuel capacities were 3.5 mL for the 100 mW unit and 10 mL for the 300 mW cell. During operation, the 99.5% methanol stored in the fuel cartridge was diluted to 10% for the power-producing reaction. The 100 mW cell could generate sufficient power for 35 h of playback time, while the 300 mW unit could operate the mp3 player for 60 h. In Oct 2009, Toshiba launched its first commercial DMFC product: Dynario™, as shown in Fig. 10. Dynario™ is used as an external power source that delivers power to mobile digital consumer products [98]. It has dimensions of $150 \times 21 \times 74.5$ mm^3 and weighs 280 g (without fuel). High concentration methanol solution is supplied as fuel in the 14 mL fuel tank, which is enough to charge a cell phone battery twice. The fuel cell outputs a 500 mA current at 5 V.

NEC [100,101] has developed miniature direct methanol fuel cells using electrodes made of carbon nanohorns, a variety of carbon nanotubes with numerous needle-like extrusions, 2–3 nm in diameter each. By attaching platinum nanoparticals to these extrusions, NEC expanded the electrode's surface area, which led to

Table 3
Passive and semi-passive direct methanol fuel cell stacks.

Investigator	Methanol concentration	Cell no. × active area	Power or power density	T (°C)	Mode An/Ca	Fuel supply techniques	Technologies
Narayanan et al. [84], 2000	1 M	6 × 3.2 cm^2	150 mW, 8 mW cm^{-2}	RT	P/P	L	Methanol was stored in the thin porous matrix in the stack reservoir. Three stacks in series were needed to power a cellular phone.
Chang et al. [85], 2002	5 M	12 × 2 cm^2	560 mW (2.8 V), 23 mW cm^{-2}	RT	P/P	L	Methanol solution was transported to the fuel cells by wicking materials and air was passively breathed from the ambient. Phase dispersed membranes based on Nafion® or Co-PTFS were applied to the MEA to decrease the methanol crossover.
Guo and Faghri [20], 2008	3 M, pure	8 × 9 cm^2	1.5 W (2.4 V, 3 M)	RT	P/P	L (3 M) V (pure)	The stack ran at 33 mA cm^2 for 57 h with 500 g 3 M methanol, generating 26.1 Wh electrical energy. The calculated fuel efficiency was 34% and the overall efficiency was 8.5%. The stack also operated under 0.2 A, 33 mA cm^2, for 64 h with 150 g methanol and 200 g water added to the thermal-fluids management system.
Cao et al. [86], 2008	2 M	8 × 2 cm^2	151 mW (1.5 V), 17.5 mW cm^{-2}	25 ± 1	0.4 mL min^{-1}/P	L	The volume and weight of the stacks are only 5.3 cm^3 and 10.7 g, respectively. The stack with double serpentine-type flow fields generated a peak output power of 151 mW at a working voltage of 1.5 V, corresponding to an average power density of 17.5 mW cm^{-2}.
Chen et al. [87,88], 2003, 2005	0.5−9.0 wt%	4 × 8 cm^2 4 × 25 cm^2	1.2 W (0.95 V, 3 wt%), 12 mW cm^{-2}	RT	P/P	L	The mobile phone could sustain 50 min with 1 mL methanol.
Liu et al. [89], 2004	1−3 M	12 × 6 cm^2	1.88 W (2.2 V, 3 M), 26 mW cm^{-2}	RT	P/P	L	The sintered stainless steel fiber felt was used as the anodic gas diffusion backing, and the reservoir of the stack was 15 cm^3.
Kim et al. [90,94], 2004, 2006	1−5 M	6 × 4.5 cm^2	1.0 W (4 M), 37 mW cm^{-2}	RT	P/P	L	The passive DMFC stack was used to power an LCD panel and a toy car. The forced air-blowing or methanol-pumping to the stack had rather negative effects of decreasing temperature and resulted in lower performance.
Guo and Faghri [16], 2006	1−5 M	4 × 4.5 cm^2 4 × 9 cm^2	870 mW (2 M) 24.2 mW cm^{-2}	RT	P/P	L	The best performance occurred when 2 and 3 M methanol solutions were used.
Baglio et al. [91], 2008	1−10 M	3 × 4 cm^2	225 mW (5 M), 20 mW cm^{-2}	RT	P/P	L	The stack with an unsupported Pt loading of 4.0 mg cm^{-2} yielded the best performance at 5.0 M operation
Chan et al. [92], 2008	2−6 M	6 × 6.25 cm^2	10.3 mW cm^{-2} (6 M)	RT	P/P	L	The DMFC stack powered a seagull display kit, 350 mW at 1.8 V, for about 4 h with 25 mL of 4 M methanol solution.

Table 4
DMFC prototype and products designs and developments with emphasis in high concentration methanol solutions.

Investigator	Prototype	Power/power density[a]	Active/passive	Methanol concentration	Technologies and performances
Motorola [95,96], 2001	4×14 cm^2	15–22 mW cm^{-2}	Active	Pure	A unique ceramic structure was used to build the DMFC stack to reduce its size and cost. Pure methanol and DI water were stored separately, and generated water was recycled to dilute the methanol.
Manhattan Scientific Inc., Energy Related Devices Inc. [97], 2002	NA	400 Wh kg^{-1}	Passive	NA	The Micro Fuel Cell achieved a specific energy output more than three times greater than standard lithium ion batteries used for cellular telephones
Motorola Labs [70,71], 2004	4×18.3 cm^2	2 W, 20 mW cm^{-2}	Active	Pure	The specific power and power density are 37 W kg^{-1} and 77 W L^{-1}, respectively. The average degradation rate was improved to 41 μV (h cell)$^{-1}$, during the over 1200 h of system lifetime test.
Toshiba [98], 2004	NA	100 mW	NA	NA	World's smallest DMFC. Dimension: $22 \times 56 \times 4.5$ mm^3; Weight: 8.5 g.
Fujitsu [99], 2004	NA	15 W	NA	30%	Aromatic hydrocarbon solid material was used as the electrolyte to reduce the methanol crossover. 300 mL 30% methanol could operate a notebook PC for 8–10 h
NEC [100,101], 2004	280 cm^2	14 W (12 V), 50 mW cm^{-2}	NA	10%	Dimension: $270 \times 270 \times 40$ mm^3; Weight: 900 g (Fuel 300 g). Electrodes were made of carbon nanohorns to increase the surface area of the catalyst.
LG Chem [102], 2005	NA	25 W	NA	NA	Weight: 1 kg; Life time: more than 4000 h One fuel cell cartridge, 200 cm^3, could power a laptop for more than 10 h.
Toshiba [103], 2005	NA	100, 300 mW	NA	99.5% methanol	Methanol was diluted to 10% during operations. The 100 mW cell can generate sufficient power for 35 h of playback time, while the 300 mW unit can operate the mp3 for 60 h.
Faghri and Guo [104], 2008	2×9 cm^2	7 mW cm^{-2} (22 mA cm^{-2})	Passive	Pure	Pure methanol and water transport from the methanol and water tanks separately with the help of wicking materials and were vaporized by an electric heater in the fuel chamber. The stack operated for 400 h at 22 mA cm^{-2} and room temperature, and the resistance was around 180 mΩ during the operation.
Sony [105,106], 2008	NA	3 W (1 W from DMFCs)	Active/passive	99%	The DMFC/Li-ion battery system generated 1.1 Wh mL^{-1} methanol. The performance decreased by 5% after 900 h operation.
Sony [107], 2009	NA	2 W from DMFC (550–600 mW cell^{-1})	Active/passive	99%	Methanol tank: 270 mL. The DMFC/Li-ion battery hybrid system generated a peak power of 10 W for the speaker. This speaker can be used for a year without refilling the tank if it is used to view DVDs for approximately two to 3 h on weekends.
Sony [107], 2009	NA	NA	Active/passive	99%	The DMFC/Li-ion battery hybrid system generated 1.37 Wh mL^{-1} methanol.
Smart Fuel Cell company [108,109], 2009	Jenny®	NA	NA	100%	Reduce the weight by up to 80% compared with lithium-ion batteries. Working temperature: −20 to 50 °C
Toshiba [98], 2009	Dynario®	2.5 W	NA	High concentration methanol solution	Dimension: $150 \times 21 \times 74.5$ mm^3; Weight: 280 g; Fuel tank: 14 mL. Unveil 3000 prototypes in Japan in 2009.
Oorja Protonics [110], 2010	OorjaPac™	NA	Active	100%	Weight: 79 kg; Volume of the methanol tank: 12 L; Operating temperature: −20 °C to 45 °C; Energy output capacity: 29 kWh day^{-1}. The OorjaPac™ Model III reduces CO$_2$ emissions by 30–66% compared with charging from the grid.
MTI Micro Fuel Cells Inc. [111–114], 2010	Mobion®	100 mW cm^{-2}	Passive	100%	Have started a global testing program. Life time: 2700 h with less than 15% degradation. Working temperature: 0–40 °C.
Tsujiguchi et al. [115], 2010	8×8.25 cm^2	1.8 W/30 mW cm^{-2} (90, 100 wt%), 800 Wh L^{-1}	Passive	70–100 wt%	Porous carbon plates were used as the methanol barrier layer. Power generation was continued for 85 h until the 12 cm^3 pure methanol was completely consumed. The volumetric energy density was calculated to be about 800 Wh L^{-1}.
Smart Fuel Cell company [116,117], 2011	EFOY® 600, 1200, 1600, 2200	25, 50, 67, 92 W	Active	100%	System efficiency: 30%. Life time: more than 3000 h

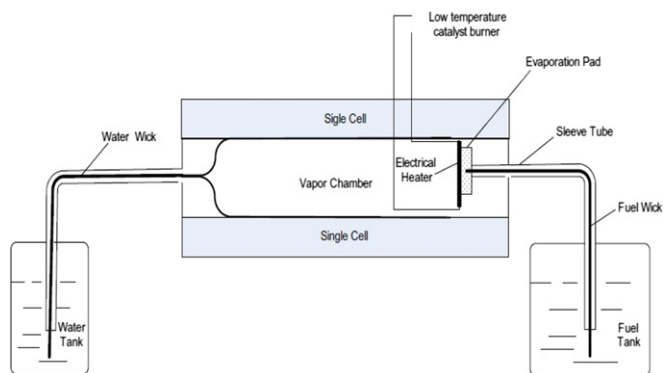[a] The performances were measured under room temperature if not mentioned otherwise.

Fig. 9. Vapor-feed DMFC stack with two cells in a series connection. Figure adopted from [100].

Fig. 11. The DMFC prototype to power laptop computers, launched by LG Chem in 2005.

an increase in the fuel cell's power generation efficiency. In 2004, the company's compact, high-powered prototype fuel cell for a laptop boasted a power density of 50 mW cm^{-2}, an average output of 14 W at 12 V, and a maximum output of 24 W. The fuel cell weighed 900 g (including 300 g fuel) and had an external dimension of $270 \times 270 \times 40$ mm^3. The fuel cell could operate for approximately 5 h on one fueling of 300 cm^3 methanol at 10% concentration.

In 2004, Fujitsu [99] announced a DMFC prototype using aromatic hydrocarbon solid electrolyte material which had about one-tenth of the methanol crossover rate encountered by typical fluorinated polymers. Consequently, high concentration methanol solution can be supplied to the product. 300 mL of 30% methanol could drive a notebook PC for 8–10 h. Furthermore, the prototype fuel cell was slimmed down to a 15 mm thickness and maintained a power output of 15 W.

LG Chem [102] unveiled a 25 W DMFC prototype to power laptop computers in 2005, shown in Fig. 11. The fuel cell was comprised of a reaction vessel and a removable 200 mL methanol fuel cartridge. One fuel cell cartridge could power a laptop for more than 10 h. LG Chem claimed that the cell itself could last for more than 4000 h. This DMFC prototype would also be able to power handheld devices such as portable media players and mobile phones by connecting to their USB ports. The fuel-cell unit weighs about 1 kg, and the temporary price was around $480 in 2005.

Sony [105,106] unveiled an ultra-small hybrid fuel cell system ($50 \times 30 \times 20$ mm^3) and exhibited the evaluation results of the system at Small Fuel Cells 2008, in Atlanta, GA. As shown in Fig. 12, the fuel cell system combined a fuel cell, Li-ion secondary battery, and a control circuit. The fuel supply, methanol with a purity of 99%, was actively controlled with a micro-pump. The peak output of the hybrid system could be as high as 3 W, while the fuel cell unit by

Fig. 10. The DMFC external power supply, Dynario™, launched by Toshiba in October 2009.

itself could only output about 1 W. The fuel cell unit generated power at a constant output and the load change in the device was handled by Li-ion rechargeable battery regulated by a control circuit. The fuel cell could be used to watch TV in a mobile phone for 14 h on 10 mL of methanol. The energy generated by the fuel cell unit with 1 mL of methanol was 1.1 Wh. The high energy efficiency resulted from a low-crossover MEA using a fullerene-based electrolyte film and a new platinum based catalyst material. Sony said that the output of the latest system decreased by only 5% after a continuous operation of 900 h.

In 2009, Sony [107] exhibited a cordless speaker system and mobile phone chargers powered by a Li-ion battery and DMFC hybrid power system at the International Hydrogen & Fuel Cell Expo (FC Expo 2009). Each DMFC single cell provided a power of 550–600 mW and the Li-ion secondary battery supplemented power when a higher power output was required. When the device required less than 550 mW, the DMFC's excess power was used to charge the Li-ion secondary battery. The cordless speaker system was driven by four DMFC single cells sharing a 270 mL methanol tank and a Li-ion battery. Four DMFCs could generate power up to 2 W. When higher output was required, the Li-ion secondary battery would provide the additional power. The maximum output of the system was about 10 W. This system can be used for a year without refilling the tank if it is used to view DVDs for about two to 3 h on weekends. Both of the mobile device chargers unveiled by Sony used USB connections. The smaller charger was equipped with a 10 mL methanol tank and had a power capacity of 13.7 Wh when combined with a 3.7 Wh Li-ion battery. It could charge a 3.4 to 4 Wh mobile phone a few times a week. The bigger charger came with a 100 mL methanol tank and allowed 25 charges in a month.

MTI Micro Fuel Cells Inc., has demonstrated the pure methanol vapor-feed, passive, DMFC Mobion® technology in prototypes and concept models in three primary product directions: external cordless rechargeable power packs, attached fuel cell power sources, and embedded micro fuel cell designs. In 2008, MTI Micro [111] unveiled a Mobion® external power pack prototype (shown in Fig. 13) with a removable methanol cartridge that can provide 25 Wh of portable power or up to 25 h of handheld power from each methanol cartridge. The charger was designed to fully charge an average cell phone battery more than 10 times from one small cartridge. The prototype contained an integrated power module with fluid conditioning that allowed the system to run in temperatures from 0 °C to 40 °C at any humidity level.

At the core of MTI Micro's compact charger prototype was its proprietary third generation Mobion Chip, only 9 cm^3. During laboratory testings in 2007, this third-generation Mobion Chip demonstrated a power output of more than 62 mW cm^{-2}, while
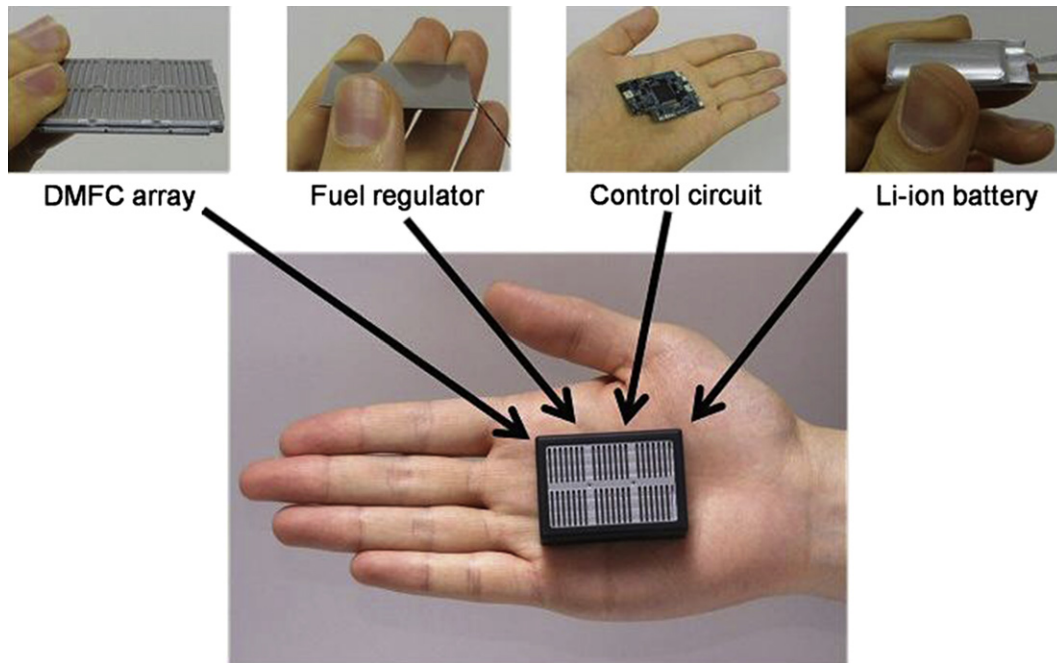
Fig. 12. The DMFC and Li-ion battery hybrid fuel cell system, launched by Sony in 2008.

producing more than 1800 Wh kg^{-1} of energy from the methanol fuel [112]. MTI Micro also announced a power density improvement of the Mobion Chip, increasing the power density to 84 mW cm^{-2} in 2009, and further increasing to 100 mW cm^{-2} in 2010 [113]. In 2008, MTI Micro Fuel Cells [114] reported that 2700 h of continuous operation with a power degradation of less than 15% was achieved with a Mobion® laboratory cell - the building block of its direct methanol Mobion chip and systems. In comparison, a typical cell phone plan in the US, marketed to moderate to heavy users including 3000 min per month, translates to only 1200 h of use over the life of a typical two-year contract.

In August 2003, SFC Smart Fuel Cell company [116] (renamed SFC Energy in July 2010 [119]) introduced users to the system SFCA25 DMFC. SFCA25 had an average output power of 25 W (600 Wh day^{-1}), maximum output of 80 W, dimensions of 465 × 290 × 162 mm^3, and weighed 9.7 kg with a fuel cartridge. The unit ran at a load of 25 W for 56 h until the 2.5 L fuel container of pure methanol was empty. The measured efficiency was 13.1% for a 25 W load, and 11.4% for 20 W. The A25 stack showed unstable operations at ambient temperatures lower than 15 °C or higher than 35 °C, according to the performance tests led by the US Army's Communications, Electronics Research Development and Engineering Center (CERDEC) [117]. Later, SFC unveiled a second generation product with a 25 W power output, the C25. The C25 was smaller, 150 × 112 × 65 mm^3, lighter, 1.1 kg, and had an orientation independent feature. SFC also introduced the SFCA50 system, with an average output power of 50 W (1200 Wh day^{-1}).

In 2006, The SFCA25 and SFCA50 were updated to the EFOY® fuel cell family. The EFOY® fuel cell family, shown in Fig. 14, had EFOY® 2200, 1600, 1200, and 600 with a charging capacity of 2.2 kWh, 1.6 kWh, 1.2 kWh, and 0.6 kWh per day, respectively. The EFOY® fuel cell, with a patented internal water-management system, was an active DMFC with water and air management. The fuel cells employ pure methanol in the fuel cartridges and dilute it to the mix ratio required for power production by the water management system. The system efficiencies are rated at 30%. The prices of the EFOY® products range from 2000 to 4000 euros. SFC warranties a 3000 h life of the system, which equates to roughly a 6

year life expectancy in a typical recreational vehicle application. SFC Energy AG sold its 20,000th EFOY® fuel cell by Jan 2011 [120].

In 2009, SFC [108] unveiled the Jenny® portable fuel cell, targeted for military use. The small size of the fuel cell and the high energy density of the methanol fuel, combined with the power management system, reduced the weight of the load carried by a soldier by up to 80% compared to packs containing conventional lithium-ion batteries. It has been proven to operate reliably, even in challenging environments with extreme temperatures (−20 °C to 50 °C) and without any performance loss at altitudes exceeding 4000 m (13,000 ft) or fully submerged under water.

Oorja Protonics, a US manufacturer of methanol fuel cells, announced the installation of 20 OorjaPac™ Model III units at Golden State Foods' Lemont, Illinois facility in 2011 [121]. The OorjaPac™ Model III, shown in Fig. 15, is equipped with a three-gallon methanol tank which can last roughly 12–16 h, and can be refueled within 1 min. The OorjaPac™ Model III [110] weighs 79 kg and can operate at temperatures ranging from −20 °C to 45 °C. It has an energy output capacity of 29 kWh day^{-1}. The OorjaPac™ Model III reduces CO$_2$ emissions by 30–66% compared with charging from the grid.

In addition to the prototypes introduced above, other companies, such as Medis [122], PolyFuel [123], Samsung SDI [124], Neah Power [125], IRD [126] etc. have also introduced DMFC prototypes for different applications. All the DMFC prototypes aim to achieve high energy density, a long lifetime, better reliablility and low cost. But all these parameters must be further improved to be commercially competitive with the current rechargeable batteries.

4. Unresolved issues

4.1. Methanol concentration sensors

In active DMFC systems, the high concentration methanol from the fuel reservoir is usually diluted with the water recovered from the cathode reaction. The diluted methanol solution supplied to the MEA should be stabilized at the optimized concentration at a given loading. The continuous change of electric loading requires rapid changes of the fuel concentration. In this circumstance, a sensitive methanol

Fig. 13. The external power pack prototype, Mobion®, unveiled by MTI Micro Fuel Cells Inc. in 2008.

sensor with a fast response time is the most critical component in the fuel cell system in order to adjust the methanol and water supply rates. Additionally, the methanol sensor should be as energy efficient and compact as possible to maximize the net output and energy density of the fuel cell system. Unfortunately, compact and accurate methanol sensors are not yet available in the market.

4.2. Carbon dioxide crossover

Jiang and Chu [127] experimentally confirmed the CO_2 crossover through a Nafion® 117 membrane in a DMFC with 2 M methanol solution. It was found that the CO_2 crossover was driven by the gas pressure gradient between the anode and the cathode of the MEA and that the crossover rate increased with an increased current density due to the higher CO_2 generation rate. In a DMFC fed with high concentration methanol, the mass transport resistance at the anode was significantly increased in order to alleviate the methanol crossover, which makes the CO_2 release from the anode more difficult. Consequently, more CO_2 will crossover through the electrolyte membrane and escape to the ambient from the cathode. The crossover of CO_2 will decrease the water back flow rate and thus decrease the cell performance. Moreover, the CO_2 will impede the O_2 transport at the cathode side and cause mass transfer limitation for the cathode reaction. Quantitative measurements of the CO_2 crossover rate in DMFCs fed with high concentration methanol solutions have never been reported.

4.3. MEA fabrication

Conventional technology fabricates the MEA by combining gas diffusion electrodes with catalyst coated membranes, followed by

Fig. 14. The EFOY® direct methanol fuel cell products, produced by SFC Energy, Inc.

a hot-pressing procedure. These methods may lead to high contact resistances between fuel cell components. Contact resistances compose 65–90% of the total resistance [128,129]. The high contact resistances at the interfaces of fuel cell components affect the heat, mass, and ionic transfers in a fuel cell or a fuel cell stack. Better methods of MEA manufacturing must be developed to enhance the catalyst utilization, decrease the contact resistance in fuel cells and cell stacks, and provide consistent experimental results.

4.4. Stack hardware and design

Miniaturization is crucial for portable applications [21,71,130,131]. Several configurations have been proposed for passive DMFC stacks [132], most commonly the bi-cell and monopolar-type. In the bi-cell type, the methanol tank is allocated between two anodes which belong to two different cells, while the cathodes of these two cells are exposed to air. Bi-cell units are grouped in a stack by leaving a gap between two cathodes belonging to two different bi-cells; the series connection of the various bi-cells is accomplished by external connections. In the monopolar configuration, all electrodes of the same type, for example, all anodes, are allocated on one face of the membrane and the cathodes on the other face. Each couple of electrodes forms a cell and all the cells share the same piece of electrolyte membrane. Series connection between two cells is created by an electric conductor passing through the membrane or by an external circuit. For both of the above two designs, the ratio between the active area and the area of the whole stack frame should be as high as possible in order to make the stack more compact and generate higher power.

4.5. Durability and cost

The durability and cost of DMFCs are also key issues that negatively impact DMFC prototypes and products [118]. Some progress has been made to lower the cost [80] and increase the lifetime [71] of the DMFC. The Department of Energy (DOE) technical targets of portable power applications (in 2013) require

Fig. 15. The OorjaPac™ Model III, manufactured by Oorja Protonics.

a lifetime of more than 5000 h, less than $300 per system cost for an under 2 W system, less than $6 per watt for a 2–25 W system, and less than $3 per watt for a 25–250 W system [133,134]. Although the lifetime of some prototypes and products, such as products from SFC and MTI, are longer than 5000 h, details about their methods are not available and the aging mechanisms of DMFCs are still not clear. More work need to be done in order to further reduce the cost and increase the lifetime of DMFCs. In the near future, lifetimes of over 5000 h and costs lower than $3 per watt will be expected.

5. Conclusions

The booming market for portable electronic devices forecasts that there will be a huge demand for portable power systems with high power density. In the years to come, DMFC technology has a good chance to prevail as a leader in this market due to its advantages of high energy density and quick refueling, crucial characteristics of portable power systems. To compete with lithium based rechargeable batteries that currently dominate the portable power market, high concentration methanol solutions (including pure methanol) should be stored in the fuel reservoir to capitalize its high energy density. However, significant progress is still needed to overcome the technical barriers in DMFCs using high concentration methanol. This paper has reviewed the fundamental studies of various topics, such as methanol crossover, water management, oxygen transport, and carbon dioxide release on DMFCs using high concentration and pure methanol in the past few years. The structural optimization principles of DMFCs using high concentration methanol have been summarized based on these studies. Advances on DMFC prototypes, products designs, and developments have also been reviewed. The development trend in recent years has been very promising. DMFC-lithium battery hybrid systems, which take advantage of both the high energy density and rapid refueling of the DMFC and the quick response to an external load from the lithium battery, have similarly shown a promising future. The state-of-the-art DMFC prototypes and products are more competitive than rechargeable batteries, especially in applications such as military uses. To make DMFC technology more appealing and the DMFC systems more competitive in the portable power market, more fundamental research must be conducted and issues such as durability and system cost should be further investigated.

References

[1] D.H. Jung, C.H. Lee, C.S. Kim, D.R. Shin, J. Power Sources 71 (1998) 169–173.
[2] S. Hikita, K. Yamane, Y. Nakajima, JSAE Rev. 22 (2001) 151–156.
[3] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc. 143 (1996) L12–L15.
[4] J.G. Liu, T.S. Zhao, Z.X. Liang, R. Chen, J. Power Sources 153 (2006) 61–67.
[5] G. Jewett, Z. Guo, A. Faghri, J. Power Sources 168 (2007) 434–446.
[6] G.Q. Lu, F.Q. Liu, C.Y. Wang, Electrochemical Solid-state Lett. 8 (2005) A1–A4.
[7] F. Liu, G. Lu, C.Y. Wang, J. Electrochem. Soc. 153 (2006) A543–A553.
[8] C. Xu, T.S. Zhao, J. Power Sources 168 (2007) 143–153.
[9] C. Xu, T.S. Zhao, Y.L. He, J. Power Sources 171 (2007) 268–274.
[10] Q.X. Wu, T.S. Zhao, R. Chen, W.W. Yang, J. Power Sources 191 (2009) 304–311.
[11] S. Kang, S.J. Lee, H. Chang, J. Electrochem. Soc. 154 (2007) B1179–B1185.
[12] X. Ren, T.E. Springer, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 92–98.
[13] X. Ren, T.E. Springer, T.A. Zawodzinski, S. Gottesfeld, J. Electrochem. Soc. 147 (2000) 466–474.
[14] J.G. Liu, T.S. Zhao, R. Chen, C.W. Wong, Electrochemistry Commun. 7 (2005) 288–294.
[15] D. Chu, R. Jiang, Electrochim. Acta 51 (2006) 5829–5835.
[16] Z. Guo, A. Faghri, J. Power Sources 160 (2006) 1183–1194.
[17] Z. Guo, A. Faghri, J. Power Sources 160 (2006) 1142–1155.
[18] K. Song, H. Lee, H. Kim, Electrochim. Acta 53 (2007) 637–643.
[19] C. Xu, A. Faghri, X. Li, T. Ward, Int. J. Hydrogen Energy 35 (2010) 1769–1777.
[20] Z. Guo, A. Faghri, Int. Commun. Heat Mass Transfer 35 (2008) 225–239.
[21] T. Ward, X.L. Li, A. Faghri, J. Power Sources 196 (2011) 6264–6273.
[22] C. Xu, T.S. Zhao, Q. Ye, Electrochim. Acta 51 (2006) 5524–5531.
[23] C. Xu, T.S. Zhao, Electrochemistry Commun. 9 (2007) 497–503.
[24] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J. Léger, J. Power Sources 105 (2002) 283–296.
[25] R. Dillon, S. Srinivasan, A.S. Aricò, V. Antonucci, J. Power Sources 127 (2004) 112–126.
[26] A. Faghri, Z. Guo, Int. J. Heat Mass. Transfer 48 (2005) 3891–3920.
[27] T.S. Zhao, C. Xu, R. Chen, W.W. Yang, Prog. Energy Combust. Sci. 35 (2009) 275–292.
[28] T.S. Zhao, R. Chen, W.W. Yang, C. Xu, J. Power Sources 191 (2009) 185–202.
[29] Q.X. Wu, Y.L. He, T.S. Zhaoa, Front. Heat Mass Transfer 2 (2011) 032001.
[30] S. Sanicharane, A. Bo, B. Sompalli, B. Gurau, E.S. Smotkin, J. Electrochem. Soc. 149 (2002) A554–A557.
[31] N. Nakagawa, K. Sekimoto, M.S. Masdar, R. Noda, J. Power Sources 186 (2009) 45–51.
[32] Y. Sone, P. Ekdunge, D. Simonsson, J. Electrochem. Soc. 143 (1996) 1254–1259.
[33] H. Kim, J. Power Sources 162 (2006) 1232–1235.
[34] M.A. Abdelkareem, N. Nakagawa, J. Power Sources 162 (2006) 114–123.
[35] W. Kim, H. Choi, Y. Lee, J. Nam, S.M. Cho, C. Chung, J. Power Sources 157 (2006) 193–195.
[36] Y.H. Pan, Electrochemical Solid-state Lett. 9 (2006) A349–A351.
[37] A. Faghri, Z. Guo, Thermal-fluid management system for direct methanol fuel cells, US Patent 7,829,211. (2010) 1–17.
[38] H. Zhang, I. Hsing, J. Power Sources 167 (2007) 450–454.
[39] Z. Guo, A. Faghri, J. Power Sources 167 (2007) 378–390.
[40] A. Faghri, Z. Guo, Vapor feed fuel cells with a passive thermal-fluids management system, US Patent 7,625,649. (2009) 1–26.
[41] M.A. Abdelkareem, N. Nakagawa, J. Power Sources 165 (2007) 685–691.
[42] Y.H. Chan, T.S. Zhao, R. Chen, C. Xu, J. Power Sources 176 (2008) 183–190.
[43] S. Eccarius, F. Krause, K. Beard, C. Agert, J. Power Sources 182 (2008) 565–579.
[44] S. Eccarius, X. Tian, F. Krause, C. Agert, J. Micromech. Microengineering 18 (2008) 104010.
[45] X.M. Ren, F.W. Kovacs, K.J. Shufon, S. Gottesfeld, Passive water management techniques in direct methanol fuel cells, US Patent 7,282,293. (2007) 1–24.
[46] C. Xu, A. Faghri, X. Li, J. Electrochem. Soc. 157 (2010) B1109–B1117.
[47] X. Li, A. Faghri, C. Xu, Int. J. Hydrogen Energy 35 (2010) 8690–8698.
[48] X. Li, A. Faghri, C. Xu, J. Power Sources 195 (2010) 8202–8208.
[49] Q.X. Wu, T.S. Zhao, R. Chen, W.W. Yang, J. Micromech. Microengineering 20 (2010) 045014.
[50] Q.X. Wu, T.S. Zhao, R. Chen, W.W. Yang, Int. J. Hydrogen Energy 35 (2010) 10547–10555.
[51] Q.X. Wu, T.S. Zhao, W.W. Yang, Int. J. Heat Mass Transfer 54 (2011) 1132–1143.
[52] M.S. Masdar, T. Tsujiguchi, N. Nakagawa, J. Power Sources 195 (2010) 8028–8035.
[53] L. Wang, Y. Zhang, Y. Zhao, Z. An, Z. Zhou, X. Liu, J. Micromech. Microengineering 21 (2011) 104012.
[54] Q.X. Wu, T.S. Zhao, Int. J. Hydrogen Energy 36 (2011) 5644–5654.
[55] Y.C. Park, D.H. Kim, S. Lim, S.K. Kim, D.H. Peck, D.H. Jung, Int. J. Hydrogen Energy 37 (2012) 4717–4727.
[56] K. Kang, G. Lee, G. Gwak, Y. Choi, H. Ju, Int. J. Hydrogen Energy 37 (2012) 6285–6291.
[57] W. Yuan, Y. Tang, X. Yang, B. Liu, Z. Wan, Int. J. Hydrogen Energy (2012) 9298–9313.
[58] Y.L. He, Z. Miao, W.W. Yang, J. Power Sources 208 (2012) 180–186.
[59] Q.X. Wu, S.Y. Shen, Y.L. He, T.S. Zhao, Int. J. Hydrogen Energy 37 (2012) 5958–5968.
[60] A.K. Shukla, P.A. Christensen, A. Hamnett, M.P. Hogarth, J. Power Sources 55 (1995) 87–91.
[61] A.S. Aricò, P. Cretì, H. Kim, R. Mantegna, N. Giordano, V. Antonucci, J. Electrochem. Soc. 143 (1996) 3950–3959.
[62] M. Hogarth, P. Christensen, A. Hamnett, A. Shukla, J. Power Sources 69 (1997) 125–136.
[63] K. Scott, W.M. Taama, P. Argyropoulos, J. Power Sources 79 (1999) 43–59.
[64] J. Kallo, W. Lehnert, R. Von Helmolt, J. Electrochem. Soc. 150 (2003) A765–A769.
[65] H. Fukunaga, T. Ishida, N. Teranishi, C. Arai, K. Yamada, Electrochim. Acta 49 (2004) 2123–2129.
[66] M.S. Masdar, T. Tsujiguchi, N. Nakagawa, J. Power Sources 194 (2009) 610–617.
[67] M.S. Masdar, T. Tsujiguchi, N. Nakagawa, J. Power Sources 194 (2009) 618–624.
[68] M.A. Abdelkareem, N. Morohashi, N. Nakagawa, J. Power Sources 172 (2007) 659–665.
[69] F. Liu, C.Y. Wang, Electrochemical Solid-state Lett. 12 (2009) B101–B102.
[70] J.W. Bostaph, D.S. Marshall, Direct methanol fuel cell including a water recovery and re-circulation system and method of fabrication, US 6,727,016. (2004) 1–10.
[71] C. Xie, J. Bostaph, J. Pavio, J. Power Sources 136 (2004) 55–65.
[72] C. Xu, A. Faghri, X.L. Li, Int. J. Hydrogen Energy (2011) 8468–8477.
[73] X.L. Li, A. Faghri, J. Power Sources (2011) 6318–6324.
[74] Y.L. He, X.L. Li, Z. Miao, Y.W. Liu, Appl. Therm. Eng. 29 (2009) 1998–2008.
[75] H. Yang, T.S. Zhao, Q. Ye, J. Power Sources 139 (2005) 79–90.

[76] J. Larminie, A. Dicks, Fuel Cell Systems Explained, first ed., John Wiley & Sons Ltd, New York, NY, 2000.

[77] R. O'Hayre, S.W. Cha, W. Colella, F. Prinz, Fuel Cell Fundamentals, first ed., John Wiley and Sons, New York, NY, 2006.

[78] M.M. Mench, Fuel Cell Engines, first ed., John Wiley and Sons, Inc, Hoboken, New Jersey, 2007.

[79] T.S. Zhao, W.W. Yang, R. Chen, Q.X. Wu, J. Power Sources 195 (2010) 3451–3462.

[80] X. Ren, P. Zelenay, S. Thomas, J. Davey, S. Gottesfeld, J. Power Sources 86 (2000) 111–116.

[81] H. Dohle, H. Schmitz, T. Bewer, J. Mergel, D. Stolten, J. Power Sources 106 (2002) 313–322.

[82] H.Y. Ha, S.Y. Cha, I.H. Oh, S.A. Hong, in: Fuel Cell Seminar 2000 Portland, Oregon, USA, 2000, p. 175.

[83] A. Oedegaard, C. Hentschel, J. Power Sources 158 (2006) 177–187.

[84] S.R. Narayanan, T.I. Valdez, F. Clara, in: Fuel Cell Seminar 2000 Portland, Oregon, USA, 2000, pp. 795–799.

[85] H. Chang, J.R. Kim, J.H. Cho, H.K. Kim, K.H. Choi, Solid State Ionics 148 (2002) 601–606.

[86] J. Cao, Z. Zou, Q. Huang, T. Yuan, Z. Li, B. Xia, H. Yang, J. Power Sources 185 (2008) 433–438.

[87] C.Y. Chen, P. Yang, Y.S. Lee, K.F. Lin, J. Power Sources 141 (2005) 24–29.

[88] C.Y. Chen, P. Yang, J. Power Sources 123 (2003) 37–42.

[89] J. Liu, G. Sun, F. Zhao, G. Wang, G. Zhao, L. Chen, B. Yi, Q. Xin, J. Power Sources 133 (2004) 175–180.

[90] D. Kim, E.A. Cho, S.A. Hong, I.H. Oh, H.Y. Ha, J. Power Sources 130 (2004) 172–177.

[91] Y.J. Kim, B. Bae, M.A. Scibioh, E. Cho, H.Y. Ha, J. Power Sources 157 (2006) 253–259.

[92] V. Baglio, A. Stassi, F.V. Matera, A. Di Blasi, V. Antonucci, A.S. Aricò, J. Power Sources 180 (2008) 797–802.

[93] Y.H. Chan, T.S. Zhao, R. Chen, C. Xu, J. Power Sources 178 (2008) 118–124.

[94] N. Hashim, S.K. Kamarudin, W.R.W. Daud, Int. J. Hydrogen Energy 34 (2009) 8263–8269.

[95] J. Bostaph, R. Koripella, A. Fisher, D. Zindel, J. Hallmark, in: Proceedings of the 199th Meeting on Direct Methanol Fuel Cell Electrochemical Society, 2001, pp. 274–285.

[96] J. Pavio, J. Hallmark, J. Bostaph, A. Fisher, B. Mylan, C.G. Xie, Fuel Cells Bull. 2002 (2002) 8–11.

[97] Energy Related Devices.http://www.energyrelatedevices.com/, 2002.

[98] Toshiba Launches Direct Methanol Fuel Cell in Japan as External Power Source for Mobile Electronic Devices (2009).http://www.toshiba.co.jp/about/press/2009-10/pr2201.htm.

[99] Fuel Cells Bull. 7 (2004) 2.

[100] Fuel Cells Bull. (2003) 4.

[101] Fuel Cells Bull. (2003) 1.

[102] T. Smith, LG to Ship Notebook Fuel Cell in 12 Months (2005).http://www.theregister.co.uk/2005/09/29/lg chem fuel cell/.

[103] T. Smith, Toshiba Touts Fuel Cell-equipped MP3 Players (2005).http://www.theregister.co.uk/2005/09/16/toshiba fuel cell mp3 players/.

[104] A. Faghri, Z. Guo, Appl. Therm. Eng. 28 (2008) 1614–1622.

[105] H. Yomogita, Sony Unveils Ultrasmall Hybrid Fuel Cell (2008).http://techon.nikkeibp.co.jp/english/NEWS EN/20080502/151303/.

[106] K. Kariatsumari, Sony Explains High Output of Ultra-small Fuel-cell System (2008).http://techon.nikkeibp.co.jp/english/NEWS EN/20080507/151383/.

[107] Toshiba, Toshiba Launches Direct Methanol Fuel Cell in Japan as External Power for Mobile Electronic Devices (2009).http://www.toshiba.com/taec/news/press releases/2009/dmfc 09 580.jsp.

[108] Fuel Cells Bull. 4 (2009) 6–7.

[109] Fuel Cells Bull. 5 (2005) 11.

[110] Oorja Protonics, OorjaPac Model III Product Sheet (2011).http://www.sfc.com/en/sfc-press-release/11236-meilenstein-sfc-energy-ag-verkauft-20.000-efoy-brennstoffzelle.html.

[111] Fuel Cells Bull. 12 (2008) 1.

[112] Fuel Cells Bull. 7 (2007) 1.

[113] Fuel Cells Bull. 12 (2009) 7.

[114] Fuel Cells Bull. 9 (2008) 7.

[115] T. Tsujiguchi, M.A. Abdelkareem, T. Kudo, N. Nakagawa, T. Shimizu, M. Matsuda, J. Power Sources 195 (2010) 5975–5979.

[116] Fuel Cells Bull. 7 (2006) 2–3.

[117] E. Bostic, N. Sifer, C. Bolton, U. Ritter, T. Dubois, J. Power Sources 137 (2004) 76–79.

[118] S.K. Kamarudin, F. Achmad, W.R.W. Daud, Int. J. Hydrogen Energy 34 (2009) 6902–6916.

[119] SFC Energy, Change of Company Name: SFC Smart Fuel Cell AG Becomes SFC Energy AG (2010).http://www.sfc.com/en/sfc-press-release/11184-neue-firmierung-aus-sfc-energy-ag-wird-sfc-energy-ag.html.

[120] SFC Energy, Milestone: SFC Energy AG Sells 20,000th EFOY Fuel Cell (2011).http://www.sfc.com/en/sfc-press-release/11236-meilenstein-sfc-energy-ag-verkauft-20.000-efoy-brennstoffzelle.html.

[121] T. Patrick, Oorja Protonics Introduces Methanol-based, On-board Battery Charger, 50 Times More Powerful Than Competition (2010).http://www.sfc.com/en/sfc-press-release/11236-meilenstein-sfc-energy-ag-verkauft-20.000-efoy-brennstoffzelle.html.

[122] Martin LaMonica, Medis Power Pack: A Fuel Cell Gadget Charge (2008).http://www.sfc.com/en/sfc press release/11236 meilenstein sfc energy ag verkauft 20.000 efoy brennstoffzelle.html.

[123] Martin LaMonica, PolyFuel to Demo Methanol Fuel Cell Laptop (2008).http://www.sfc.com/en/sfc-press-release/11236-meilenstein-sfc-energy-ag-verkauft-20.000-efoy-brennstoffzelle.html.

[124] Samsung SDI, DMFC System for Military (2011).http://www.sfc.com/en/sfc-press-release/11236-meilenstein-sfc-energy-ag-verkauft-20.000-efoy-brennstoffzelle.html.

[125] Neah Power, Neah Power Homepage (2011).http://www.neahpower.com/.

[126] IRD Fuel Cell Technology, Direct Methanol Fuel Cell (DMFC) (2011).http://www.ird.dk/index.php?id=76,0,0,1,0,0.

[127] R. Jiang, D. Chu, Electrochemical Solid-state Lett. 5 (2002) A156–A159.

[128] T. Swamy, E.C. Kumbur, M.M. Mench, J. Electrochem. Soc. 157 (2010) B77–B85.

[129] E. Sadeghi, N. Djilali, M. Bahrami, J. Power Sources 196 (2011) 246–254.

[130] J.H. Wee, J. Power Sources 173 (2007) 424–436.

[131] S.K. Kamarudin, W.R.W. Daud, S.L. Ho, U.A. Hasran, J. Power Sources 163 (2007) 743–754.

[132] W. Qian, D.P. Wilkinson, J. Shen, H. Wang, J. Zhang, J. Power Sources 154 (2006) 202–213.

[133] H. Dinh, T. Gennett, Novel Approach to Advanced Direct Methanol Fuel Cell Anode Catalysts (2009). 1–12, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/dinh-gennett topic 5a dmfc nrel kickoff.pdf.

[134] Donna Lee Ho, John Kopasz, Thomas Benjamin, Walter Podolski, U.S. Department of Energy Efforts in Portable Power (2010). 1–26, http://www.fuelcellseminar.com/media/5171/lrd41-1_ho.pdf.